NITROSYLATION AND THIONITROSYLATION REACTIONS OF SOME RUTHENIUM COMPLEXES

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to the

DEPARTMENT OF CHEMISTRY

INDIAN INSTITUTE OF TECHNOLOGY, KANPUR

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Dedicated to
My Parents
As a token of
Love and Regards.

STATEMENT

I hereby declare that the matter embodied in this thesis is the result of investigations carried out by me in the Department of Chemistry, Indian Institute of Technology, Kanpur, India, under the supervision of Professor U.C. Agarwala.

In keeping with the general practice of reporting scientific observations, due acknowledgement has been made wherever the work described is based on the findings of other investigators.

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CERTIFICATE

Certified that the work contained in this thesis entitled: "NITROSYLATION AND THIONITROSYLATION REACTIONS OF SOME RUTHENIUM COMPLEXES", has been carried out by Ms. Minu Gupta, under my supervision, and the same has not been submitted elsewhere for a degree.

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PREFACE

One of the most interesting and important areas in which contemporary inorganic chemists may profitably contribute has been the chemistry of organometallic compounds. For the past fifteen years, the chemistry of $[Ru(\eta^5-C_5H_5)Cl(PPh_3)_2]$ has been developed by a number of chemists. Systems have been synthesized focusing on the patterns of the reactions of different complexes in terms of donor and acceptor properties of the bonded ligands and the subtle changes within the coordination sphere of the metal ions. The nitrosylation reactions of triphenylphosphine cyclopentadienyl complexes and their derivatives have recently been carried out and it was realized that the complexes with ligands having different σ-donor and π-acceptor properties like $AsPh_3$, $SbPh_3$, heterocyclic molecules should behave differently towards nitrosylation of the complexes. If a systematic study of the complexes $[Ru(\eta^5-C_5H_5)-X(EPh_3)_2]$ (E = As, Sb; X = $\bar{Cl}$, $\bar{Br}$, $\bar{I}$, $\bar{CN}$, $\bar{NCS}$, $\bar{SnCl_3}$) and their N-heterocyclic derivatives with NOX (X = Cl^-, Br^- or Br_3^-) were carried out, it may provide a deeper insight into the correlation of the electronic effects of the ligands with the reaction patterns and into the factors responsible for the changes in the reaction medium.

Another interesting area worth probing into is the synthesis and reactivity of metal thionitrosyls. The development of the

chemistry of metal thionitrosyl is still in infancy, despite the fact that the attention has been drawn to the use of $N_3S_3Cl_3$ as a potential thionitrosylating agent. It was, therefore, thought to be of interest to carry the reactions of metal complexes with $N_3S_3Cl_3$ and the substitution reactions of thionitrosyl complexes with N-heterocyclic ligands in the search of finding a general procedure for the syntheses of metal thionitrosyls.

An area which has not been explored so far by any chemist is the reactions of coordinated NS group with various nucleophiles and electrophiles. These reactions will make an interesting study because of the difference in their behaviour from that of metal nitrosyls.

The subject matter of the first chapter reflects the scope and the objective of the work described in the thesis. The brief overview regarding the syntheses, reactivity and the bonding in metal nitrosyl complexes which could adequently account for some of their physico-chemical properties, has also been presented therein. In addition, a very brief overview of the chemistry of thionitrosyls has also been given therein.

Chapter two encompasses the results of the reactions of $[Ru(\eta^5-C_5H_5)(EPh_3)LX]$ and $[Ru(\eta^5-C_5H_5)(EPh_3)L-L]^+X^-$ (E = As, Sb; L-L = 2,2'-bipyridine, 1,10-phenanthroline; L = pyridine, γ-picoline, $AsPh_3$, $SbPh_3$, PPh_3; X = Cl^-, Br^-, I^-, CN^-, NCS^-) with NOX (X = Cl^-, Br^- or Br_3^-) yielding $[Ru(NO)X_nY_{3-n}(EPh_3)L]$ (n = 0-3) or $[Ru(NO)X_2(EPh_3)L-L]^+X^-$ (X = Cl^- or Br^-). It contains the

the interpretative discussion of the analytical and spectral data of the reaction products in which NO binds to metal as NO^+ with a loss of C_5H_5 group.

The reaction products described in chapter three have resulted from the reactions of $[Ru(\eta^5-C_5H_5)SnCl_3(EPh_3)L]$ or $[Ru(\eta^5-C_5H_5)(EPh_3)(L-L)]^+SnCl_3^-$ (L = py, γ-pic, $AsPh_3$, $SbPh_3$, PPh_3; L-L = 2,2'-bipy, 1,10-phen) with NOX (X = Cl^-, Br^- or Br_3^-). Under the conditions, two parallel reactions occurred simultaneously. These are (1) formation of nitrosyl (2) formation of the complexes in which one of the EPh_3 (E=As,Sb) group is bonded to the metal ion through the π-electrons of one of the phenyl rings and NO as NO_2 after oxidation. The difference in the reactivities of phosphine, arsine and stibine complexes towards NOX was also discussed in the same chapters.

Chapter IV deals with the syntheses of a few thionitrosyl complexes of ruthenium. The reactions of trithiazyltrichloride with Ru(III) complexes having coordinated solvent molecules $[RuCl_3(EPh_3)_2S]$ (E = P, As; S = solvent) afforded $[Ru(NS)Cl_3(EPh_3)$ The substitution reactions of $[Ru(NS)Cl_3(EPh_3)_2]$ with $E'Ph_3$ (E' = P, As, Sb) and N-donor heterocyclic base have also been described therein.

The products discussed in chapter V have been the results of reactions of EPh_3 (E = P, As) towards $[Ru(NS)Cl_3(EPh_3)_2]$ in different solvents (benzene, chloroform, toluene, xylene). It was

summarized that the first step in these reactions has been the attack of EPh_3 on the sulfur atom of the coordinated NS group which further rearranges to some other polymeric or ring compounds.

The last chapter deals with a brief summary of the work presented in the thesis, along with a few related problems for future studies.

CONTENTS

		page
STATEMENT	... ...	iii
CERTIFICATE	... ...	iv
CERTIFICATE OF COURSE WORK	... ...	v
ACKNOWLEDGEMENTS	... ...	vi
PREFACE	... ...	viii
CHAPTER – I :	Introduction ...	1
CHAPTER – II :	Reactions of NOX ($X = Cl^-$, Br^- or Br_3^-) with cyclopentadienyl Ruthenium Complexes ...	69
CHAPTER – III :	Reactions of NOX ($X = Cl^-$, Br^- or Br_3^-) with cyclopentadienyl Ruthenium Complexes having trichlorostannate as coligand ...	102
CHAPTER – IV :	Reactivity of $[RuCl_3(EPh_3)_2S]$ (E = As, P; S = CH_3CHO, DMSO, DMF, THF, CH_3CN, $(CH_3)_2CO$, CS_2) with trithiazyltrichloride and substitution reactions of $[Ru(NS)Cl_3(EPh_3)(E'Ph_3)]$ (E = As, P; E' = As, P, Sb) ...	126
CHAPTER – V :	Reactions of EPh_3 (E = P, As) with coordinated NS group of $[Ru(NS)Cl_3(EPh_3)_2]$ in different solvents ...	145
CHAPTER VI :	Summary and Scope for future work ...	171

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CHAPTER I

INTRODUCTION

1.1 Scope and Objective

In 1969 Wilkinson and his coworkers[1] isolated the cyclopentadienyl complex of ruthenium $[Ru(\eta^5-C_5H_5)Cl(PPh_3)_2]$ which was later synthesized by another facile route by Bruce and Windsor[2] (1977). Since then the rapidly growing area of organometallic chemistry has attracted many chemists who developed the chemistry of this molecule.[3-6] The pronounced steric interaction and the presence of high electron density on the metal ion resulting from two bulky PPh_3 molecules have become responsible for its unusual chemistry. Systems have been synthesized which focus the reaction pattern for different complexes and are relevant for the rationalization of their stability in terms of donor and acceptor propertie of the bonded ligands and the subtle changes within the coordination sphere of the metal ion. Generally two approaches have been

applied in their synthetic reactions.

(a) Those which centered around the substitution of chloride ion by other anions or by neutral ligands to yield cationic derivatives $[Ru(\eta^5-C_5H_5)L(PPh_3]^+$.

(b) Those in which one of the PPh_3 molecules is substituted by other ligand molecule, e.g. the reactions of hydrides or alkyls with alkynes.

Although the synthetic area has been extensively explored during past twenty years, survey of the literature indicates that in most of these reactions emphasis has been laid on the reactions with unsaturated organic molecules resulting in the formaion of unusual π and σ-bonded complexes.[7-10] Almost all their reactions have been carried out with its phosphine derivative. One should, however, not overlook the fact that the complexes having PPh_3 substituted by other ligands with different σ donor/π-acceptor properties may not only change the course of reactions but may provide a deeper insight into the electronic effects responsible for the synthetic reactions.

Recent work[11-13] has included the reactions of $[Ru(\eta^5-C_5H_5)(PPh_3)_2Cl]$ with a large number of heterocyclic bases, $AsPh_3$ and $SbPh_3$. These studies not only hold the promise of revealing that one of the PPh_3 molecules is easily replaceable by the heterocyclic bases and the substitution of second PPh_3 takes place under extrem conditions but they also reveal that the course of reactions of

NOX with $SnCl_3^-$ complexes $[Ru(\eta^5-C_5H_5)(PPh_3)_2SnCl_3]$[14] differs from those of $[Ru(\eta^5-C_5H_5)(PPh_3)_2X]$ where X is any anion except $SnCl_3^-$. This poses an interesting question of the part played by $SnCl_3^-$ ion (strong π-acceptor) in changing the course of reaction and yield $[Ru(NO_2)SnCl_3(PPh_3)(\pi-C_6H_5)PPh_2]$. No clear picture has yet emerged out regarding the cause of this difference. Empirically it seems to be certain that the reaction path is dependent upon a delicate balance of various electronic or/and steric factors of the reactants. This prompted us to extend the study of these reactions further. Another important question regarding these reactions is ''why is the basic character of the phosphorus atom of the π-bonded phosphine $[(\pi-C_6H_5)PPh_2]$ towards other metal centre lost to the extent that it remains uncoordinated with the metal ion The key to understand such question may be found in the results of the reactions of NOX with the complexes $[Ru(\eta^5-C_5H_5)SnCl_3LL']$ where LL' are ligands with different donor/acceptor properties. It has now been well established that there exists a gradual variation in σ-basic and π-acid characters of P, As, Sb in EPh_3 and other heterocyclic molecules.[15] On account of this variation, it may be possible to find factors responsible for the changes in the reaction path, if a systematic study of these reactions are carried out with analogous molecules having Co-ligands like $AsPh_3$, $SbPh_3$ and/or other heterocyclic bases. Results of these reactions may contribute, though a little, to the understanding of the aforesaid problems and it may be worthwhile to examine the reactions of NOX

with $[Ru(\eta^5-C_5H_5)SnCl_3(EPh_3)L]$ or $[Ru(\eta^5-C_5H_5)(EPh_3)L-L]^+SnCl_3^-$ (E = As, Sb; L = $AsPh_3$, $SbPh_3$, PPh_3, pyridine, γ-picoline, L-L = 2,2'-bipyridine, 1,10-phenanthroline) and characterize the reaction products.

Furthermore, the structure, the bonding and the reactivity of transition metal nitrosyls have been a provocative subject for the many years. NOX (X = Cl^-, Br^- or Br_3^-) has previously been used to introduce nitrosyl functionality into organometallic complexes.[16-20] It generally reacts by simple oxidative addition mechanism. Some attention has also been paid in the past regarding the reactions of cyclopentadienyl ruthenium complexes with NOX effecting the substitution of cyclopentadienyl ligand by NO and X (X = Cl^- or Br^-).[14] Since triphenylphosphine is a better π-acid and because of its smaller size it places the phenyl group nearer to the metal center, thereby offering a greater steric hindrance compared to $AsPh_3$, $SbPh_3$[21] and other heterocyclic derivatives. We wish to explore the reactions of NOX with the cyclopentadienyl complexes of ruthenium, the latter molecules as coligands.

The second problem which interested us the most for the past several years is the synthesis and reactivity of metal thionitrosyls. In our earlier papers,[20,22,23] we have reported the reactions of $N_3S_3Cl_3$ with $RuCl_3$, $[RuCl_2(PPh_3)_3]$, $CoH[P(OPh)_3]_4$ etc. which gave us an impression that $N_3S_3Cl_3$ can be used as a thionitrosylating agent. However trithiazyltrichloride is air sensit

and unstable in different solvents. It has now been well established that depending upon the reaction conditions it interacts with metal salts or complexes affording various interesting products containing NS^+, N_2S_2, $N_2S_2^{2-}$, $N_3S_2^{2-}$, $NSCl^{2-}$, NSCl etc. as coligands.[24] Although attention has been drawn to the use of NSCl as a synthetic potential for metal thionitrosyls, yet all attempts have been plagued by problems of still undefined reaction conditions, under which it is able to act as thionitrosylating agent.NO suggestion has yet been made in this direction. The problem is, therefore, still in an embryonic state. For want of the reaction conditions and for our own interest in the ligand exchange reactions as potential synthetic approach for metal thionitrosyls, we thought it interesting to examine (1) the reactions of $N_3S_3Cl_3$ with ruthenium complexes having coordinated solvent molecules and (2) the substitution reactions of $[Ru(NS)Cl_3(EPh_3)_2]$ and $[Ru(NS)Cl_3(EPh_3)(E'Ph_3)]$ (E = P, As; E' = P, As, Sb) with various heterocyclic molecules.

It is well known that a number of metal ions (Cr, Mo, W, Mn, Tc, Re, Ru, Os, Co) form thionitrosyl complexes. Despite their syntheses, the literature survey indicates no work regarding the reactions of coordinated NS by nucleophiles and electrophiles. Because of our expectation of behavioural difference of coordinated NS towards nucleophiles or electrophiles compared

to those of metal nitrosyls, it is felt that such a study should be an interesting one. Though the progress in this direction may be a slow one due to the difficulty in structural characterization of the products, an initiative is warranted in this direction.

With these aims under consideration, we have carried out the following:

(i) <u>Reactions of η^5-cyclopentadienyl ruthenium complexes $[Ru(\eta^5-C_5H_5)(EPh_3)LX]$ where E = As, Sb; L = Pyridine, γ-Picoline, $AsPh_3$, $SbPh_3$, PPh_3) and $[Ru(\eta^5-C_5H_5)(EPh_3)$-L-L]X (E = As, Sb; L-L = 2,2'-Bipyridine, 1,10-Phenanthroline, X = Cl^-, Br^-, I^-, CN^-, NCS^-) with NOX (X = Cl^-, Br^- or Br_3^-)</u>

The reactivity of NOX(X = Cl^-, Br^- or Br_3^-) with the various cyclopentadienyl ruthenium(II) complexes is described in chapter II. In cases where X = Cl^-, Br^-, I^-, CN^-, NCS^- in the η^5-cyclopentadienyl ruthenium(II) complexes, nitrosyl complexes of the type $[Ru(NO)XX'_2(EPh_3)L]$ and $[Ru(NO)XX'(EPh_3)L\text{-}L]X$ were isolated and characterized (where L = py, γ-pic, $SbPh_3$, $AsPh_3$, PPh_3; X=X'=Cl or Br; L-L = 2,2'-bipyridine, 1,10-phenanthroline). The difference in the reactivity of the cyclopentadienyl complexes of triphenylphosphine, triphenylarsine and triphenylstibine towards NOX has also been discussed therein. The results form the contents of chapter II.

(ii) Reactions of NOX($X = Cl^-$, Br^- or Br_3^-) with η^5-cyclopentadienyl ruthenium(II) complexes $[Ru(\eta^5-C_5H_5)(EPh_3)L.(SnCl_3)]$ and $[Ru(\eta^5-C_5H_5)(EPh_3)L-L]^+SnCl_3^-$ (where E = As, Sb; L = Pyridine, γ-Picoline, $AsPh_3$, $SbPh_3$, PPh_3; L–L = 2,2'-Bipyridine, 1,10-phenanthroline)

The reactions of NOX ($X = Cl^-$, Br^- or Br_3^-) with trichlorostannate ruthenium complexes $[Ru(\eta^5-C_5H_5)(EPh_3)L\ SnCl_3]$ or $[Ru(\eta^5-C_5H_5)(EPh_3)L-L]^+SnCl_3^-$ give interestingly nitrito complexes with a possible π-interaction of one of the phenyl rings of triphenylarsine and triphenylstibine ligand with ruthenium metal $[Ru(NO_2)SnCl_3(EPh_3)\{(\pi-C_6H_5)EPh_2\}]$. The conversion of NO to NO_2 under mild reaction conditions and affectively blocking of a vacant coordination site by one of the phenyl rings of triphenylarsine or triphenylstibine in the complexes is fascinating. The trichlorostannate complexes of $[Ru(\eta^5-C_5H_5]LL'SnCl_3]$ with $AsPh_3$ and $SbPh_3$ as coligands behave differently towards NOX compared to those of triphenylphosphine. This forms the contents of chapter III of the thesis.

(iii) Reactivity of $[RuCl_3(EPh_3)_2S]$ E = As, P; S = DMSO, DMF, THF, $(CH_3)_2CO$, CS_2, CH_3CN, CH_3CHO) towards trithiazyl trichloride and substitution reactions of $[Ru(NS)Cl_3(EPh_3)(E'Ph_3)]$ (E = As, P; E' = As, P, Sb)

Trithiazyl trichloride $N_3S_3Cl_3$ reacts with $[RuCl_3(EPh_3)_2S$

to form $[Ru(NS)Cl_3(EPh_3)_2]$ and $[Ru(NS)Cl_3(EPh_3)(E'Ph_3)]$. Chapter III describes the results of these reactions and those of the ligand substitution reactions of $[Ru(NS)Cl_3(EPh_3)_2]$ and $[Ru(NS)Cl_3(EPh_3)(E'Ph_3)]$ with ligands like $E'Ph_3$ (E''=P, As, Sb) and N-donor heterocyclic bases.

(iv) Reaction of EPh_3 (E = P, As) with coordinated NS group of $[Ru(NS)Cl_3(EPh_3)_2]$ in different solvents

The reactions of EPh_3 with $[Ru(NS)Cl_3(EPh_3)(E'Ph_3)]$ were considered with a view to examine the results of the nucleophilic attack of EPh_3 on the sulphur (electrophile) of the bonded NS group in benzene and in other non-coordinating solvents. The reactions of $[Ru(NS)Cl_3(EPh_3)_2]$ (E = P, As) in different solvents were also carried out. The preliminary results of these reactions have been described in chapter V.

Chapter VI summerizesthe results of all the reactions alor with a few proposals for the possible future work.

Considering the fascinating aspects of the syntheses and versatility of the nitrosyl and thionitrosyl ligands reactivity with ruthenium complexes, it will be appropriate to have a brief overview of the work done so far with this molecules, which has been described under the following heads:

1.2 CHEMISTRY OF TRANSITION METAL NITROSYLS

A number of review articles treating different aspects of metal nitrosyl complexes have already appeared in the literature.[25-32] A few of these are comprehensive,[25,27,33] while others are specialized dealing with the structures and bonding of metal nitrosyls,[28,29] their synthetic aspects and the reactions of coordinated nitrosyl group.[31,34,35] A review regarding the application of transition metal nitrosyls in pollution control and organic synthesis has also appeared.[36] Despite these reviews, it will not be inappropriate to consider very briefly the present position concerning the synthesis, reactivity and bonding of metal nitrosyls.

1.2.A Synthetic Routes

Ten pathways for the synthesis of metal nitrosyls have been described. These are (1) direct insertion of NO (2) reactions of ionic nitrosonium salts (3) reactions of NOX ($X = Cl^-$, Br^-, Br_3^-, NO_2^-), (4) reactions of alkyl and alkali metal nitrites, (5) reactions of nitrosoamines, (6) reactions of hydroxyl amine, (7) reactions of nitric acid, (8) reactions of bis(triphenylphosphine)nitrogen (+1) nitrite and (9) reactions of transition metal nitrosyls and (10) reactions of S-nitrosoderivatives. Out of these routes the first has been widely used while the potential of third, fourth, fifth, eight, ninth & tenth are now under widespread investigation.

A.1 Nitric Oxide

There are many strong attributes that favour the use of nitric oxide as nitrosylating agent to synthetic chemists. These include its easy availability, higher product yield with concomitantly fewer side reaction products, mild reaction conditions etc. However, nitric oxide has several disadvantages too, the important ones being its oxidizing property and thermodynamic instability. Limitations of this nature have motivated the development of new approaches for introducing NO into the coordination sphere of metal complexes, preferably by adopting a way which might totally avoid the direct use of nitric oxide.

A.1(a) Addition of Nitric Oxide

The reaction is expected for complexes in which the metal is having either 17 or 15 electron configuration, lacking one or three electrons from the inert gas configuration. Since NO can add one or three electrons in making the M-NO bond, the metal ion achieves the inert gas configuration. A facile introduction of NO is thus possible in such metal complexes.

$$[CoCl_2L_2] + NO \longrightarrow [Co(NO)Cl_2L_2] \qquad [37]$$

($L = 2e^-$ donor neutral ligand)

A.1(b) Substitution of ligands of nitric oxide

The demand to achieve an $18e^-$ configuration can also be met by the substitution of ligands equivalent to 3 electrons or even by reductive nitrosylation. Some representative examples are,

$$[M(CO)_3Cl_2L_2] + NO \longrightarrow [M(NO)_2Cl_2L_2] \qquad [38]$$

(M = Mo, W)

$$[RuH_4L_3] + NO \longrightarrow [Ru(NO)_2L_2] \qquad [39]$$

In some cases, the introduction of NO may however not lead to an inert gas configuration like in the following examples where a fourteen electron system becomes a fifteen electron one.

$$[Fe(chel)_2] + NO \longrightarrow [Fe(NO)(chel)_2] \qquad [28]$$

(chel = dithiocarbamate, dimethyl glyoxime, a schiff base or porphyrin.

In case the precursor complex is short of only one electron from the inert gas configuration, an $18e^-$ system shell is achieved by substituting a two e^- donor by NO where the latter acts as a three electron donor.

$$[OsCl_3(SbPh_3)_3] + NO \longrightarrow [Os(NO)Cl_3(SbPh_3)_2] \qquad [40$$

$$[V(CO)_6] + NO \longrightarrow [V(CO)_5NO] \qquad [41$$

Reaction pattern becomes more complex when precursor metal complex is short of an even number of electrons (usually two) from the inert gas configuration. Under these conditions, two nitrosyl groups may substitute producing a coordinatively saturated species.

$$[Rh(CO)_2Cl_2] \longrightarrow [Rh(NO)_2Cl]_n \qquad [42]$$

Interestingly, in such cases a metal-metal bond is sometimes formed

$$[H_3IrCl_2] + NO \longrightarrow [Ir(NO)_2L]_2 \qquad [43]$$

(Ir-Ir distance = 2.717 Å with no bridging group present in the dimer).

$$[CpRu(CO)_2Cl] + NO \xrightarrow[\text{irradiation}]{\text{UV}} [CpRu(NO)Cl_2] \qquad [44]$$

$$[CpCoC_2H_4] + NO \xrightarrow{\text{hexane}} [Cp_3Co_3(\mu_3\text{-}NO)_2] \qquad [45]$$

A.1(c) Reductive Nitrosylation

Nitric oxide with an unpaired electron in its π^*-orbital could also function as a reducing agent during nitrosylation reaction. Higher halides of molybdenum and tungsten are among several systems which undergo reductive nitrosylation.[46-48]

$$[MoCl_4(CH_3CN)_2] + NO \longrightarrow [Mo(NO)_2Cl_2(CH_3CN)_2] + 2\ NOCl$$

$$[WCl_6] + NO \longrightarrow [W(NO)_2Cl_2]$$

A.2 Nitrosonium ion (NO^+) as nitrosylating agent

Salts of NO^+X^- ($X^- = BF_4^-$, PF_6^- etc) can also be used to synthesize metal nitrosyls. Nitrosylation of the metal ions in these reactions proceeds either by addition or substitution process. However, owing to moisture sensitivity of these salts, the reactions are generally carried out in the inert solvents.

$$[Rh(CO)X(PPh_3)_2] \xrightarrow{NO^+} [Rh(NO)_2(PPh_3)_2] \qquad [49]$$

Though the application of nitrosyl salts for nitrosylation can be categorized under the addition or the substitution reactions, oxidative addition can also occur in coordinatively unsaturated substrates, e.g.

$$[RhCl(PPh_3)_3] + NO^+ \longrightarrow [Rh(NO)(PPh_3)_3Cl]^+ \qquad [50]$$

$$[M(\eta^5\text{-}C_5H_5)(CO)L] + NO^+ \longrightarrow [M(\eta^5\text{-}C_5H_5)(NO)L]^+ \qquad [51]$$

(M = Co, Rh)

$$Mo(CO)_6 + NO^+PF_6^- \xrightarrow{CH_2Cl_2} [Mo(NO)_2(PF_6)_2] \qquad [52]$$

$$\xrightarrow{CH_3NO_2} [Mo(NO)_2(CH_3NO_2)_4][PF_6]_2$$

$$\Big\downarrow \text{L} = CH_3CN,\ OPPh_3,\ 2,2'\text{-Bipyridine},$$

$$[Mo(NO)_2L_4]X_2 \qquad X = PF_6$$

$$[(COD)Ir(\pm\mu\text{-}pz)]_2 \xrightarrow{NOBF_4} [(COD)_2Ir_2(\mu\text{-}pz)NO]BF_4 \qquad [53]$$

(Ir–Ir distance = 3.224 Å)

Treatment of metal cluster, $[Ru_3(CO)_9(PPh_3)_3]$ in CH_2Cl_2/Et_2O with NO^+ results in the formation of $[Ru(NO)(CO)_2(PPh_3)_2]^+$. Recently NO^+ has been demonstrated to be the most successful nitrosylating reagent for the transition metal carbonyl clusters.

$$[HM_3(CO)_{11}]^- + NO^+ \longrightarrow HM_3(CO)_{10}(NO) + CO \qquad [54]$$

(M = Ru, Os)

$$[H_3Os_4(CO)_{12}]^- + NO^+ \xrightarrow[THF]{CH_2Cl_2} [H_3Os_4(CO)_{12}NO] \qquad [55]$$

A.3 <u>NOX (X = Cl^-, Br^-, Br_3^- or NO_2^-) as nitrosylating agent</u>

Oxidative addition reactions of NOX with metal complexes, in which the coordination number of the metal center is either increased by the addition of NO and X or remains the same after the substitution of ligand molecules by NO and/or X, have provided a successful route to the synthesis of many nitrosyls. Reactions are in general carried out at ordinary temperature. Out of the large number of examples depicting the use of NOX, a few are given below.

$$[RuCl_2L_4] + NOCl \longrightarrow [Ru(NO)Cl_3L_2] \qquad [56]$$

$$[M(CO)_6] + NOCl \longrightarrow [M(NO)_2Cl_2]_n \qquad [57]$$

(M = Mo, W)

$$[M(CO)_6] + NOBr \longrightarrow [M(NO)Br_2] \qquad [58]$$

(M = W, Mo)

$$[Ir(CO)Cl(PPh_3)_2] + NOBr_3 \longrightarrow [Ir(CO)(NO)Br_2(PPh_3)_2] \qquad [59]$$

$$[Ru(NS)Cl_3L_2] + NOBr_3 \longrightarrow [Ru(NO)Br_2ClL_2] \qquad [60]$$

$$[R(CO)_2RuCl] + NOCl \xrightarrow{CH_2Cl_2} [R(NO)RuCl_2] \qquad [61]$$

R = pentamethylcyclopentadienyl

$$[Ru(\eta^5\text{-}C_5H_5)X(PPh_3)_2] + NOX' \longrightarrow [Ru(NO)XX'_2(PPh_3)_2] \qquad [14,62]$$

$X' = Cl^-, Br^-, Br_3^-, NO_2^-$

$X = Cl^-, Br^-, I^-, CN^-, NCS^-, SnCl_3^-$

Recently, convenient route for the synthesis of complex $(NH_4)_2[Ru(NO)Cl_5]$ involves reaction of $RuCl_3.XH_2O$ with NOCl in ethanolic medium in the presence of TPP.

$$RuCl_3.XH_2O + NOCl \xrightarrow[TPP]{EtOH} (NH_4)_2[Ru(NO)Cl_5] \qquad [63]$$

A.4 Nitrites as a source of NO

Study of the synthetic nitrosylating reactions indicates that the potential of alkyl nitrites for introducing NO in metal complexes has been utilized to a negligible extent and it needs further study, in order to understand more about its potential. A few of the known examples are,

$$[MCl_3.XH_2O] + PPh_3 + \eta\text{-Pentyl nitrite} \longrightarrow [M(CO)Cl_3(PPh_3)_2] \quad [64$$

$$[NiX_2(PPh_3)_2] + NaNO_2 \longrightarrow [Ni(NO)X(PPh_3)_2] \quad [65$$

$(X = Cl^-, Br^-, I^-, NO_3^-)$

$$[RhCl(PPh_3)_3] + KNO_2 \xrightarrow[MeOH]{AcOH/HClO_4} [Rh(NO)(NO_2)(PPh_3)_2] \quad [66$$

The underlying reaction pathway for nitrosylation by NOX shows th following equilibrium.

$$NO_2^- + 2\,H^+ \rightleftharpoons H_2O + NO^+$$

Godwin and Meyer have successfully distinguished between the above reaction (attack of NO^+ generated by acidic solution of nitrite salt on metal complexes) and the coordination of NO_2^-, followed by oxygen abstraction ,using the following reactio

$$[Ru(LL)_2(H_2O)X]^+ + NO_2^-/H^+ \longrightarrow [Ru(NO)(LL)_2X]^{2+} \quad [6$$

(LL = OPhen, Bipy)

$$RuCl_3.XH_2O + \eta\text{-Butyl nitrite} \xrightarrow{PPh_3} [Ru(NO)Cl_3(PPh_3)_2] \qquad [68]$$

$$CoCl_2.6H_2O + \text{methyl/ethyl nitrite} \xrightarrow[LiClO_4]{\text{Bipyridyl}} [Co(bipy)_2(NO)Cl]ClO_4 \qquad [69]$$

A.5 <u>N-Nitrosoamines</u>

N-methyl-N-nitroso p-toluene sulfonamide (MNTS) reacts with a number of metal hydrido complexes to produce metal nitrosyls. In this reaction, a hydride ion (formally a one e^- donor) along with a two e^- donor ligand is replaced by the nitrosyl group resulting in the fixation of linear nitrosyl group.

$$[MHCl_2L_3] + MNTS \longrightarrow [M(NO)Cl_2L_2] \qquad [70]$$

(M = Rh, Ir)

$$RuCl_3.XH_2O + PPh_3 + MNTS \xrightarrow{EtOH} [Ru(NO)Cl_3(PPh_3)_2] \qquad [71]$$

Two types of mechanism for nitrosylation by nitrosoamines have been envisaged.[34]

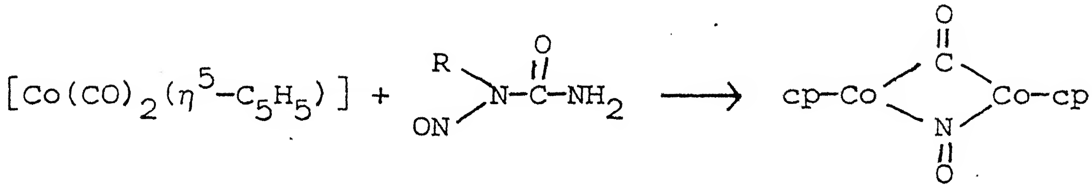
A significant new variant on the use of MNTS has been reported by Legzdins and Grease.[72] The nitrosoamine acts as a formal source of NO for the following carbonyl anions.

$$[cpM(CO)_3]^- \longrightarrow [cpM(CO)_2(NO)]$$

(M = Cr, Mo, W)

$$[\pi\text{-}C_3H_5)Fe(CO)_3]^- \longrightarrow [(\pi\text{-}C_3H_5)Fe(CO)_2(NO)]$$

In an interesting reaction, N-nitroso alkyl urea reacts to yield a complex having one carbonyl and one nitrosyl bridge.[73]



Use of N-nitroso derivatives as nitrosylating agent involves <u>in situ</u> generation of NO, thereby totally avoiding the direct use of gaseous nitric oxide and offers a simple one step synthesis of transition metal nitrosyls. In these reactions, the cleavage of the weak N-NO bond generates NO which is subsequently picked up by the metal ions for the nitrosylation reactions.

$$[MCl_3,XH_2O] + DPNA \xrightarrow[\text{ethylenediamine}]{\text{in the presence of } PPh_3,\ AsPh_3,} [M(NO)Cl_3(PPh_3)_2] \qquad [89]$$

(M = Ru, Rh, Ir)

A.6 Hydroxyl amine as a source of NO

Hieber and coworkers first exploited the use of hydroxyl amine as nitrosylating agent in 1948. Since then, it has been widely used as reductive nitrosylating agent.[74–76] It is interesting to note that it could be used as nitrosylating agent in alkaline, neutral as well as acidic medium.[77] The interesting observation, however, is that the complexes synthesized by hydroxyl amine method under acidic, neutral and alkaline conditions,

invariably are linear M–NO, as is evident from the X-ray crystal structure data.

$$[MX(NO)L_4]^{2+} + L \xrightarrow{NH_2OH} [MX(NO)L_4]^{+} \qquad [78]$$

(M = Ru, Fe; X = Cl^-, Br^-; L = py, O-phenylene bis dimethylarsine)

This reaction is the first to produce a $(M\text{–}NO)^{2+}$ group.

A.7 Nitric acid as nitrosylating agent

Concentrated nitric acid is useful, particularly, in producing nitrosyl complexes in higher oxidation states. The identity of nitrosylating species during the course of reactions still remains obscure. Generally nitrosylation reaction appears to proceed by oxidative addition of $NO^+NO_3^-$. A few of the following examples support this view.

$$[ReH_3L_4] + HNO_3 \longrightarrow [Re(NO)_2L_2(NO_3)_2] \qquad [79]$$

$$[M(CN)_6]^{4-} + HNO_3 \longrightarrow [M(NO)(CN)_5]^{2-}$$

(M = Fe, Ru, Os)

$$RuCl_3.xH_2O + HNO_3 \xrightarrow{NaCN} Na_2[Ru(CN)_5NO].2H_2O \qquad [80]$$

A.8 Bis(triphenylphosphine)nitrogen (+1) nitrite [PPN(NO$_2$)]

Bis(triphenylphosphine)nitrogen (+1) nitrite has recently

been found to be particularly successful as a mild reagent for converting metal carbonyls into nitrosyl carbonyl complexes. $PPN(NO_2)$ has been used to prepare nitrosyl clusters.

$$[YCCo_3(CO)_9] + PPN(NO_2) \xrightarrow[\text{or acetonitrile}]{\text{THF/acetone}} PPN[YCCo_3(CO)_7(NO)] \quad [81]$$

(Y = Me, Ph, COOH, $C_5H_5Fe(C_5H_4)$)

$$[Os_{10}C(I)_2(CO)_{24}] + PPN(NO_2) \longrightarrow CO + CO_2 + [Os_{10}C(I)(CO)_{22}(NO)] \quad [82]$$

$$Ru_5C(CO)_{15} + PPN(NO_2) \xrightarrow[\text{room temp.}]{\text{THF}} [PPN]Ru_5C(CO)_{13}(NO)] \xrightarrow[CH_2Cl_2]{AuPR_3} [Ru_5C(CO)_{13}(NO)AuPR_3] \quad [83]$$

Other reactions of $PPN(NO_2)$ are also known.[84]

$$Fe(CO)_5 + PPN(NO_2) \longrightarrow (PPN)[Fe(NO)(CO)_3] + CO_2 + CO$$

A.9 Transition metal nitrosyls as nitrosylating agent

Cobalt dinitrosyl halides have recently been utilized successfully as nitrosylating agents for syntheses of transition metal complexes.[85,86] $[CoX(NO)_2]_2$ ($X = Cl^-, Br^-, I^-$) react with carbonyl hydrido phosphine vanadium complexes to yield $[V(NO)_2(THF)_4]X$ and $[V(CO)_3(NO)dppe)]$ in dark.

$$[VH(CO)_4dppe] + [CoX(NO)_2]_2 \xrightarrow{\text{THF}} [V(NO)(CO)_3dppe] \quad [87]$$

$$[V(NO)(CO)_3dppe] \downarrow [V(NO)_2(THF)_4]X$$

dppe = $Ph_2PCH_2CH_2PPh_2$

A few other representative reactions under this category where coordinated NO of one nitrosyl complex has been exploited for nitrosylation of others, are given below

$$[Rh(NO)(PPh_3)_3] + [CoCl_2(PPh_3)_2] \longrightarrow [RuCl(PPh_3)_3] + [Co(NO)Cl(PPh_3)_2] \quad [88]$$

A.10 Reactions of S-Nitroso derivatives

Recently, new development in the direction of synthesis of metal nitrosyls was the reactions of metal salts and complexes with S-nitroso derivatives. The S-nitrosoderivatives which were used as nitrosylating agents, undergo dissociation reactions ($2\ RS{-}NO \longrightarrow R{-}S{-}S{-}R + 2\ NO$) at varying temperature depending upon the organic moiety linked to the sulphur.[90]

$$RuCl_3 \cdot xH_2O + \text{S-Nitrosocysteine} \xrightarrow[\text{of } PPh_3]{\text{in the presence}} [Ru(cys\text{-}cys)_2Cl(NO)]$$

$$CoCl_2 \cdot 6H_2O + \text{S-Nitrosocysteine} \xrightarrow[\text{2,2'-Bipyridine}]{LiClO_4} [Co(bpy)_2Cl(NO)]ClO_4$$

$$Mo(CO)_6 + PT \xrightarrow[Cl_2 \text{ gas}]{PPh_3} [\{MoCl_2(PPh_3)_2\}_2N_2O_2]Cl_2 \quad [91]$$

1.2.B Reactivity of transition metal nitrosyls

The recent upsurge in the study of transition metal nitrosyls and the reactions of the nitrosyl ligand is partly due to increase in understanding the way in which NO binds to a metal. Because of the presence of an extra electron in NO, it binds to the metals in modes not yet observed for CO in metal carbonyls. As has been cited previously, it functions both as an electron donor (NO^+) or an electron acceptor (NO^-), depending upon the nature of metal ion. In some cases, the bonding may be as $N_2O_2^{2-}$. Consequently, the mode of bonding determines the partial charges that develop on the nitrogen and oxygen centers of the bonded NO, resulting in the interesting variation in its reactivity.[33] It has been demonstrated that the complexes having linear M–N–O with (ν_{NO}) greater than 1850 cm^{-1} undergo nucleophilic reactions, while those with bent M–N–O, electrophile reactions.[92] Another important reason for investigating the coordinated NO reactivity stems largely from the attempts to remove or to diminish the NO concentration in the exhaust gases, which has an important bearing on pollution control. Furthermore, there exists a definite possibility of forming organo-nitrogen compounds using nitric oxide in reactions assisted by transition metal catalysts. Table 1.1 through 1.6 summarize the results of the reactions of metal nitrosyls with nucleophiles (OH^-, N_3^-, NCO^-, OEt^-, NH_3^-, N_2H_4, NH_2OH, $ArNH_2$ etc) and electrophiles (HCl, $PhCH_2Br$, O_2 etc). The results of the

Table I.1 Reactions of the nitrosyl complexes of osmium

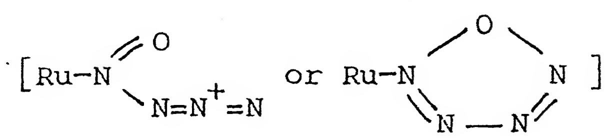
Reactant	Reagent	Product	Notes	Reference
1	2	3	4	5
1. $[Os(NO)(CN)_5]^{2-}$	OH^-	$[Os(CN)_5(NO_2)]^{4-}$		[31]
2. $[Os(NH_3)_5(NO)]^{3+}$	OH^-	$[Os(NH_3)_4(NH_2)(NO)]^{2+}$ + H_2O		[35]
3. $[Os(NO_2)(PPh_3)_2]$	2 HCl	$[OsCl_2(NHOH)(NO)$-$(PPh_3)_2]$		[31]
4. $[Os(CO)(NO)Cl(PPh_3)_2]$	HCl	$[Os(CO)Cl_2(HNO)$-$(PPh_3)_2]$		[31]
5. $[Os(NO)_2(PPh_3)_2]$	O_2	$[Os(NO)(NO_3)O_2(PPh_3)_2]$	In absence of acid	[93]
6. $[Os(NO)_2(PPh_3)_2]$	O_2	$[Os(NO)_2(OH)(PPh_3)_2]^+$	In presence of acid	[93]
7. $[Os(NO)Cl(diars)_2]^{2+}$	2 OH^-	$[OsCl(diars)_2(NO_2)]$ + H_2O	diars = O-phenylenebis-(dimethyl)arsine	[35]
8. $[Os(NO)Cl(diars)_2]^{2+}$	N_2H_4	$[OsCl(diars)_2N_3]$ + H_2O + $2H^+$		[35]
9. $[Os(NO)Cl(diars)_2]$	NH_2NHPh	$[OsCl(diars)_2$-$\{N(O)NNHPh\}]$ + $2H^-$		[35]

...cont

Table I.1 (contd.)

1	2	3	4	5
10. $[NH_4][Os(NO)Cl_5]$	Ammonia solution	trans-$[Os(NO)(NH_3)_4OH]Cl_2$ $\xrightarrow{NH_4X}$ trans-$[Os(NO)(NH_3)_4OH]X_2$	Reactant and reagent heated in ammonia solution. Product precipitated with $(NH_4)_2CO_3$	[94]
11. $[OsCl_5(NO)]^{2-}$	HL	$[OsCl_3LNO]^-$	HL = pyridine-2-carboxylic acid	[95]

Table I.2 Reactions of the nitrosyl complexes of ruthenium

Reactant 1	Reagent 2	Product 3	Notes 4	Reference 5
1. $[Ru(NO)Cl(Bipy)_2]^{2+}$	OH^-	$[Ru(NO_2)Cl(Bipy)_2]^{2+}$	Bipy = 2,2'-bipyridine	[67]
2. $[Ru(NO)Cl(Bipy)_2]^{2+}$	$ArNH_2$	$[RuCl(Bipy)_2(NNAr)]^{2+}$	Ar = p-RC_6H_4; R = H, CH_3 or CH_3O	[96]
3. $[Ru(NO)Cl(Bipy)_2]$	C_6H_5NRMe	$[RuCl(Bipy)_2\text{-}N(=O)C_6H_4NRMe]^+$		[97]
4. $[Ru(NO)Cl(Bipy)_2]$	N_3^-	$[RuCl(Bipy)_2(H_2O)]^+ + N_2 + H_2O$		[98]
5. $[Ru(NO)Cl(Bipy)_2]$	NH_3	$[Ru(NO_2)Cl(Bipy)_2]^{2+}$		[67]
6. $[Ru(NO)Cl(diars)_2]^{2+}$	OH^-	$[Ru(diars)_2Cl(NO_2)]^{2+}$		[99]
7. $[Ru(NO)Cl(diars)_2]^{2+}$	N_3^-	$[Ru(diars)_2Cl(N_3)] + N_2O + N_2$	The intermediate involved in the reaction has been proposed to bound to metal either as 	[100]
8. $[Ru(NO)Cl(diars)_2]^{2+}$	N_2H_4	$[RuCl(N_3)(diars)_2]$		[99]
9. $[Ru(NO)Cl(diars)_2]^{2+}$	$PhNHNH_2$	$[RuCl(diars)_2\{N(O)NNHPh\}]$		[99]

...contd

Table I.2(contd.)

1	2	3	4	5
10. $[Ru(NO)Cl(diars)_2]^{2+}$	NH_3	$[Ru(NO_2)Cl(diars)_2]^{2+}$		[99]
11. $[Ru(NO)(CN)_5]^{2-}$	OH^-	$[Ru(NO_2)(CN)_5]^{4-}$		[31]
12. $[Ru(NH_3)_5(NO)]^{3+}$	OH^-	$[Ru(NH_2)(NH_3)_4(NO)]^{2+}$ $+[Ru(NH_3)_5(N_2)]^{2+}$ or $[Ru(NH_3)_5(NO_2)]^{2+}$ or $[Ru(NH_3)_5(NO)(OH)]^{2+}$	Products are OH^- concentration dependent	[101]
13. $[Ru(NH_3)_5(NO)]^{3+}$	RNH_2	$[Ru(NH_3)_5(N_2)]^{2+}$ + ROH	R = Me or Et Reaction occurs at pH = 10	[102]
14. $[Ru(NH_3)_5(NO)]^{3+}$	NH_3	$[Ru(NH_3)_4(NO)(OH)]^{2+} + N_2O + N_2$ or $[Ru(NH_3)_5(N_2)]^{2+}$		[31]
15. $[Ru(NH_3)_5(NO)]^{3+}$	N_2H_4	$[Ru(NH_3)_5(N_2O)]^{2+}$ and/or $[Ru(NH_3)_5(N_2)]^{2+} + [Ru(NH_3)_5(N_3)]^{2+}$	Product, temperature dependent	[93]
16. $[Ru(NH_3)_5(NO)]^{3+}$	NH_2OH	$[Ru(NH_3)_5(N_2O)]^{2+} + N_2O + N_2$		[103]
17. $[Ru(NO)_2(PPh_3)_2]$	HCl	$[RuH(NO)_2(PPh_3)_2]^+ \longrightarrow [Ru(NO)Cl_3(PPh_3)_2]$	In the absence of oxygen	[93]

...contd.

Table I.2(contd.)

1	2	3	4	5
18. $[Ru(NO)_2(PPh_3)_2]$	$PhCH_2Br$	$\{[Ru(CO)(NO)Br(PPh_3)_2]$ and/or $[RuBr_2(CO)_2(PPh_3)_2]\}$ + PhCN + $PhCONH_2$ + PhCN=NOH	At 110°C temperature and under CO atmosphere in toluene	[104]
19. $[Ru(NO)_2(PPh_3)_2]$	O_2	$[Ru(NO)(NO_3)(O_2)(PPh_3)_2]$	In absence of acid	[93]
		or		
		$[Ru(NO)_2(OH)(PPh_3)_2]^+$	In presence of acid	
20. $[Ru(CO)(NO)X(PPh_3)_2]$	O_2	$[Ru(NO)(O_2)(PPh_3)_2X]$	X = Cl or NCS	[105]
21. $[Ru(NO)(O_2)(NCS)(PPh_3)_2]$	$2PPh_3$	$[Ru(NO)(O_2)(NCS)(PPh_3)_2]$ +2 $O=PPh_3$		[106]
22. $[Ru(\eta^3-C_3H_5)(NO)(PPh_3)_2]$	CO	$[Ru(\eta^3-C_3H_5)(CO)(NO)(PPh_3)_2]$ + $[Ru(CO)_3(PPh_3)_2]$ + acrolein oxime		[107]
23. $[Ru(NH_3)_5(NO)]^{3+}$	e^-	$[Ru(NH_3)_5(NO)]^{2+}$	Reversible reaction	[108]
24. $[Ru(NH_3)_5(NO)]^{3+}$	Cr^{2+} + H^+ + H_2O	$[Ru(NH_3)_6]^{2+}$		[109]
25. $[Ru(NO)Cl_5]^{2-}$	Alk. HCHO	$[Ru_2N(OH)_5(H_2O)_5].nH_2O$		[110
26. $[Ru(NO)Cl_5]^{2-}$	$SnCl_2$/ HCl	$[Ru_2Cl_8N(H_2O)_2]^{3-}$		[123]

...contd.

Table I.2(contd.)

1	2	3	4	5
27. $[Ru(OH)(NO_2)_4(NO)]^{2-}$	2 OH^-	$[Ru(OH)(NO_2)_5]^{4-}$ + H_2O		[35]
28. $[Ru(NO)X_5]^{2-}$	$h\nu, H_2O$	$[Ru(H_2O)X_5]^{2-}$ + NO	Photolysis in aq. solution, X = Cl, Br or I, reversible reaction	[111]
29. $[Ru(NO)Cl(Bipy)_2]^{2+}$	$h\nu, CH_3CN$	$[RuCl(CH_3CN)(Bipy)_2]^{2+}$ + NO	Reversible reaction, photolysis in CH_3CN medium	[111]
30. $[Ru(NO)_2(PPh_3)_2Cl]^+$	Cl^-	$[Ru(NO)Cl_3(PPh_3)_2]$	Excess Cl^- ions; Fate of NO is not known	[112]
31. $[Ru(NO)Cl(O_2)(PPh_3)_2]$	2 CO	$[Ru(NO_3)(CO)_2Cl(PPh_3)_2]$		[94]
32. $[Ru(NO)_2(PPh_3)_2]$	$h\nu$, CO	$[Ru(CO)_4(PPh_3)_2]$ + CO_2 + N_2O	24 hours reaction under 100 atmosphere in presence of CO	[113]
33. $[Ru(NO)Cl_3(PPh_3)_2]$	PPh_3	$[Ru_4(\mu\text{-}PPh_2)_4(\mu\text{-}Cl)_4(NO)_4]$	In reduction condition	[114]
34. $[Ru(NO)Cl_3(H_2O)]$	Glycine (gly)	$K[Ru(gly)(OH)_3(NO)]$		[115]
35. $[Ru(NO)(NO_3)_x]^{(3-x)+} \cdot YH_2O$	2,2'-Bipy	$[Ru(NO)(NO_3)_z]^{(3-z)+}$ and $[Ru(NO)(bpy)_2NO_3]^{2+}$	2,2'-Bipy = 2,2'-Bipyridine in presence of aq. HNO_3 absence of reducing agent	[116]
36. $[Ru(NO)(NO_3)_x]^{(3-x)+} \cdot YH_2O$	2,2'-Bipy	$[Ru(NO)(bpy)(NO_3)]^{2+} \xrightarrow{+e} [Ru(NO)(bpy)_2NO_3]^{2+}$	In presence of reducing agent	[116]

...contd.

Table I.2(contd.)

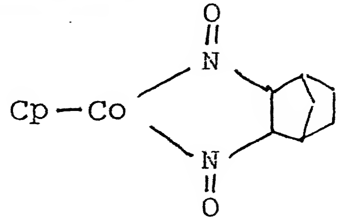
1	2	3	4	5
37. $Na_2Ru(CN)_5NO.2H_2O$	OH^-, SH^-, SO_3^{2-}, NH_3, N_2H_4	$[Ru(CN)_5H_2O]^{3-}$		[80]
38. $[RuX(NO)L_4]^{2+}$	NH_2OH	$[RuX(NO)L_4]^+$	X = Cl or Br L = Pyridine or O-phenyl-enebis(dimethylarsine)	[117]
39. $[Ru_3(CO)_{10}(\mu_2\text{-}NO)_2]$	CO, 1 atm 110^oC	$[Ru_3(CO)_{12}]$, $Ru_3(CO)_{10}(\mu_2\text{-}NO)$, $(\mu_2\text{-}NCO)$, $[Ru_4N(CO)_{12}\mu_2\text{-}L]$	Via the intermediate $[Ru_3N(CO)_{10}NO]$	[118]
40. $[RuCl_5(NO)]^{2-}$	HL	$[RuCl_2L_2(NO)]$	HL = Pyridine-2-carboxylic acid	[115]
41. $[Ru(NO)_2L_2]$	$PhCH_2Br$	$[RuBr(CO)NOL_2]$, $[RuBr_2(CO)_2L_2]$, PhCH:NOH, PhCN, $BzNH_2$, PhCHO, $PhCH_2OH$	L = PPh_3 under CO in refluxing PMe_3	[119]
42. $[Ru(NO)_2L_2]$	$PhCH_2Br$	$[RuBr_2(NCPh)_2L_2]$, $[RuBr_3(NO)L_2]$, PhCN, $BzNH_2$, $PhCH_2CH_2Ph$, PhCHO	In the absence of CO	[119]

Table I.3 Reactions of the nitrosyl complexes of cobalt

Reactant	Reagent	Product	Notes	Reference
1	2	3	4	5
1. $[Co(diars)_2(NO)](ClO_4)_2$	HBr	$[Co(diars)_2Br(HNO)]^{2+}$	Br^- acting as lewis base	[120]
2. $[Co(NO)(PPh_3)_3]$	HCl	$[Co(NO)Cl_2(PPh_3)_2]$ + $[CoCl_2(PPh_3)_2]$		[121]
3. $[Co(NO)(PPh_3)_3]$	C_6H_5COCl	$[Co(NO)(CO)(PPh_3)_2]$ + C_6H_5Cl + PPh_3		[122]
4. $[Co(NH_3)_5(NO)]^{2+}$	Cr^{2+}	$[Cr(H_2O)_6]^{3+}$ + NO		[109]
5. $[Co(NO)_2(PPh_3)_2]$	BH_4^-	$[Co(NO)(PPh_3)_3]$ + NH_3		[123]
6. cis-$[Co(en)_2(NO)$-$(MeOH)]Cl_2$	NO	cis-$[CoCl(NO_2)(en)_2]Cl$ + N_2O	In MeOH	[124]
7. $[Co(NO)(PPh_3)_3]$	7 NO	$[Co(NO)_2(NO_2)(PPh_3)]$ + 2 O = PPh_3 + $2N_2O$ + $\frac{1}{2}N_2$		[125]
8. $[Co(NO)(CO)_3]$	NO	$[Co(N_3O_4)]_n$ + $[Co_4(NO)_8$-$(NO_2)_3(N_2O_2)]$	n = ∞ in solid; n = 2 in solution	[126]

...contd.

Table I.3 (contd.)

1	2	3	4	5
9. $[Co(\eta^5\text{-}C_5H_5)(\mu\text{-}NO)]_2$	Norbornene		In NO atmosphere $C_p = (\eta^5\text{-}C_5H_5)$	[127]
10. $[Co(NO)(DMG)_2]$	$[RhCl(PPh_3)_3]$	$[Rh(NO)(PPh_3)_3]$ + $[Rh(NO)\text{-}Cl_2(PPh_3)_2]$ + $[CoCl(DMG)_2L]$	L = Lewis base associated with the reagent	[128]
11. $[Co(NO)(DMG)_2]$	$[RhH(CO)\text{-}(PPh_3)_3]$	$[Rh(CO)(NO)(PPh_3)_2]$ + $[Rh(NO)(PPh_3)_3]$ (trace amount) + $[CoCl(DMG)_2L]$	L = Lewis base associated with the reagent	[128]
12. $[Co(NO)(diars)_2]^{2+}$	NCS^-	$[Co(NO)(diars)_2(NCS)]^+$		[129]
13. $[(\eta^5\text{-}C_5H_5)Co(NO)]^{2-}$	Na/Hg	$Na^+[(\eta^5\text{-}C_5H_5)Co(NO)]^- \xrightarrow[\text{THF}]{\text{MeI } (-40^\circ C)} [(\eta^5\text{-}C_5H_5)Co(Me)(NO)]$	In Et_2O	[130]
14. $[Co(CO)_3NO]$	$CH_2CHCHCH_2$, (C_4H_6), UV radiation	trans $\eta^2\text{-}C_4H_6Co(CO)_2NO$ cis $\eta^4\text{-}C_4H_6Co(CO)NO$	In ligand xenon solution	[131]

...contd.

Table I.3 (contd.)

1	2	3	4	5
15. $[Co(NO_2)(NH_3)_5]^{2+}$	Cr^{2+}	$Co^{2+} + [CrONO(H_2O)_5]^{2+}$		[132]
16. $[cpCo(\mu_2NO)]_2$	NHR	$[cp_2Co_2(\mu_2\text{-}NO)(\mu_2\text{-}NHR)]$	R = t C_4H_9	[133]

Table I.4 Reactions of the nitrosyl complexes of rhodium

Reactant	Reagent	Product	Notes	Reference
1	2	3	4	5
1. $[Rh(NO)(NCMe)_2(PPh_3)_2]^{2+}$	OH^-	$[Rh(NO)(OH)(PPh_3)_2]^+$		[134]
2. $[Rh(NO)(PPh_3)_3$	HCl	$[RhCl_3(NH_2OH)(PPh_3)_2]$ $\xrightarrow{CO}$ $[Rh(CO)Cl_3(PPh_3)_2]$	Excess HCl	[121]
3. $[Rh(NO)(PPh_3)_3]$	C_6H_5COCl	$[Rh(CO)Cl(PPh_3)_2]$ + PPh_3	Via $[RhCl(COPh)(NO)(PPh_3)_2]$	[122]
4. $[Rh(NO)(PPh_3)_3]$	p-$MeC_6H_4SO_2Cl$	$[RhCl(PPh_3)_3]$ + [p-$MeC_6H_4SO_2]_2$		[122]
5. $[Rh(NO)Cl_2(PPh_3)_2]$	$AlHBu^t_2$ + PPh_3	$[RhCl(PPh_3)_3]$		[122]
6. $[RhClL_3]$	NO	$[RhCl(NO)(NO_2)L_2]$ + N_2O + L	L = PPh_3 or $AsPh_3$	[135]
7. $[Rh(NO)_2(PPh_3)_2]^+$	4 CO	$[Rh(CO)_3(PPh_3)_2]^+$ + N_2O + CO_2	Product reacts with NO to regenerate the reactant	[113, 136]
8. $[Rh(NO)(PPh_3)_2L]$	Alkene	$[Rh(NO)(PPh_3)_2(alkene)]$	Excess alkene, Alkene = 1-hexene, cyclohexene, styrene L = p-benzoquinone	[137]

Table I.5 Reactions of the nitrosyl complexes of iridium

Reactant	Reagent	Product	Notes	Reference
1	2	3	4	5
1. $[Ir(NO)X_5]^{2-}$	OH^-	$[Ir(NO_2)X_5]^{3-}$	X = Cl, Br	[138]
2. $[Ir(NO)Cl_3(PPh_3)_2]^+$	OEt^-	$[IrCl_3\{N(=O)OEt\}(PPh_3)_2]$		[139]
3. $[Ir(NO)(NCMe)_2(PPh_2)_3]^{2+}$	OH^-	$[Ir(NO)(OH)(PPh_3)_2]^+$		[134]
4. $[Ir(NO)X_5]^{2-}$	NH_3	$[Ir(NH_3)Cl_5]^{2-} + N_2$	X = Cl, Br	[138]
5. $[Ir(NO)X_5]^{2-}$	N_3^-	$[IrCl_5(H_2O)]^{2-} + N_2 + N_2O$	Aqueous medium	[138]
6. $[Ir(NO)X_5]^{2-}$	NH_2OH	$[IrCl_5(H_2O)]^{2-} + N_2O$	Aqueous medium	[138]
7. $[Ir(NO)(PPh_3)_3]$	HCl	$[IrCl_3(NH_2OH)(PPh_3)_2] \xrightarrow{CO} [Ir(CO)Cl_3(PPh_3)_2]$	Excess HCl	[121]
8. $[Ir(NO)_2(PPh_3)_2]^+$	O_2	$[Ir(NO)(NO_3)(PPh_3)_2]$		[158]
9. $[IrBr(NO)_2(PPh_3)_2]$	3(CO)	$[IrBr(CO)_2(PPh_3)_2] + CO_2 + N_2O$		[112]
10. $[Ir(CO)(NO)(PPh_3)_2]$	PPh_3	$[Ir(NCO)(PPh_3)_3]$	In presence of the UV light	[113]
11. $[IrBr(NO)_2(PPh_3)_2]$	NO	$[IrBr(NO)(NO_2)(PPh_3)_2] + N_2O$		[112]

...contd.

Table I.5 (contd.)

1	2	3	4	5
12. $[Ir(CO)(NO)XCl(PPh_3)_2]$ (X = Cl, Br, I, NCS, NCO, N_3)	O_2	$[Ir(CO)(NO_3)XCl(PPh_3)_2]$	In C_6H_6 at 25 °C rate of reaction decreases with X as I > Br > Cl > NCS > NCO > N_3	[140]
13. $[Ir(NO)Cl_3(PPh_3)_2]^+$	ROH	$[IrCl_3(PPh_3)_2N(O)OR]^+ + H^+$	R = C_2H_5 or CH_3	[139]
14. $[Ir(NO)(CH_3CN)_3(PPh_3)_2][PF_6]$ (dppn = 3,6-bis-(2'-pyridyl)pyridazine)	dppn/$CuCl_2$-$\cdot xH_2O$	$[IrCl(PPh_3)_2(\mu\text{-dppn})(\mu\text{-NO})\text{-}CuCl][PF_6]$		[141]
15. $[Ir(NO)(MeCN)_3(PPh_3)_2]$-$[PF_6]$	9,10-phenanthrenequinonediimine (H_2L)	$[Ir(NO)(H_2L)(PPh_3)_2][PF_6]$		[142]
16. $[IrCl(NO)L_2]^+$ (L = PPh_3)	Tetra-allyltin	$[Ir(NO)(\eta^3\text{-}C_3H_5)L_2]^+$	At 0 °C	[143]
17. $[(COD)_2Ir_2(\mu\text{-pz})_2NO]BF_4$	CO(g)	$[(COD)_2Ir_2(\mu\text{-pz})_2(NO)(CO)]BF_4$		[53]
18. $[(COD)_2Ir_2(\mu\text{-pz})_2NO]BF_4$	HCl	$[(COD)_2Ir_2(\mu\text{-pz})_2(\mu\text{-NO})Cl_2]BF_4$		[53]

Table I.6 Reactions of the nitrosyl complexes of molybdenum

Reactant	Reagent	Product	Notes	Reference
1	2	3	4	5
1. $[Mo(NO)_2(S_2CNEt_2)_2]$	N_3^-	$[Mo(NO)(S_2CNEt_2)_3] + N_2O + [Mo(NO)(N_3)(DMSO)(S_2CNEt_2)_2]$	In DMSO	[144]
2. $[Mo(NO)_2(S_2CNEt_2)_2]$	NCO^-	$[Mo(NO)(S_2CNEt_2)_2] + [Mo(NO)(NCO)(DMSO)(S_2CNEt_2)_2]$		[144]
3. $[Mo(NO)_2Cl_2]_n$	Heat(340–350°C)	$[MoOCl_4] + MoO_2Cl_2 + Mo + N_2O + N_2$		[145]
4. 3 cis-$[Mo(NO)_2(S_2CNR_2)_2]$	UV radiations	$2[Mo(NO)(S_2CNR_2)_3] + 2\ N_2O + MoO_2$	On irradiation of the reactant the reaction proceeds via formation of a dimeric hyponitrite intermediate– $[(ON)(R_2NCS_2)_2Mo-\{N(O)N(O)\}Mo(S_2CNR_2)_2(NO)]$	[146]
5. $K_4[Mo(NO)(CN)_5]$	HCl/CsCl	$Cs_2[Mo(NO)Cl_5]$		[147]

...contd

Table I.6 (contd.)

1	2	3	4	5
6. $[Mo(\eta^5-C_5H_5)(NO)_2Cl]$	$Na[AlH_2-(OCH_2CH_2-OMe)_2]$	$[(\eta^5-C_5H_5)Mo(NO)_2H]$	In toluene	[148]
7. $[(\eta^5-C_5H_5)Mo(NO)_2H]$	Ph_3C^+ or tropylium ion	$[(\eta^5-C_5H_5)_2Mo_2(NO)_4H]^+$	In CH_2Cl_2 Reactant: Reagent, 2:1	[149]
8. $[Mo(NO)_2Cl_2]_n$	L or L_2	$[Mo(NO)_2L_2Cl_2]$	L = CH_3CN, PhCN, PPh_3 or Py L_2= 2,2'-Bipyridyl, 1,2-bis(diphenyl-phosphinoethane)	[150]
9. $[Mo(NO)_2(CH_3NO_2)_4](PF_6)_2$	L	cis-$[Mo(NO)_2L_4]X_2$ $\downarrow$ Na/Hg, Li/Et_3BH, Na[Ph_2CO] in CH_3CN or THF $[Mo(NO)_2L_2]_2^{2+}$	L = CH_3CN, OPh_3, 2,2'-Bipyridine, 0.5 $Ph_2PCH_2CH_2PPh_2$ X = PF_6, BF_4 L_2= 2,2'-Bipyridine, 3,4,7,8-tetramethyl 1,10-phenanthroline	[52]

reduction, insertion and other reactions undergone by transition metal nitrosyls specially those of osmium, ruthenium, cobalt, rhodium, iridium and molybdenum are also described therein.

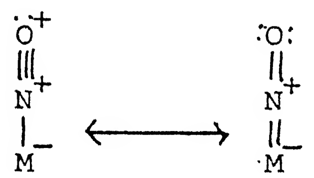
1.2.C <u>Bonding modes of Nitric Oxide coordinated to Transition metals</u>

Nitrosyl group, in transition metal complexes is generally bonded through nitrogen. Although substantial evidence has been accumulated for metal nitrogen coordination, the bonding through oxygen atom can-not, however be ruled out. A large number of X-ray diffraction studies on the metal nitrosyls point out the following three types of principal bonding modes.

1. <u>Terminal linear M-N-O</u>

In this mode of bonding, it is assumed that there is first the transfer of unpaired π-electrons from NO to the metal atom, followed by the formation of sigma bond as a result of interaction of the lone pair of electrons on nitrogen of NO^+ with the metal orbital. σ-bond thus formed, is further reinforced by the π-back donation from metal to π^* orbitals of NO^+. Thus, under this scheme, NO acts formally as three electron donor ligand. From the MO description, it is apparent that the π-bonding description leads to the linear mode of coordination. However, the wide variation of properties of NO in this type of coordination is misleading

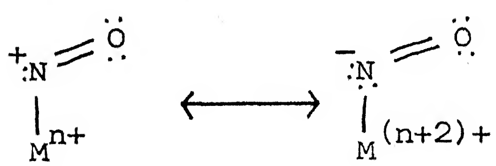
which can only be rationalised by the valence bond model. Accordingly, nitrogen under this scheme is sp hybridized with M-N-O bond angle in range 175-180^{o}. The multiple bond character



of M-N bond is in agreement with the observed short M-N distance.

2. Terminal bent M-N-O

This type of bonding occurs where the M-N-O bond is not colinear. In these cases the NO^+ is believed to behave as a lewis acid, and accepts an electron pair from the metal (base). It suggests that NO can be treated formally as one e^- donor and the resulting species should be NO^-. In terms of the valence bond representation the bonding mode could be written by the following two canonical forms (nitrogen atom is in sp^2 hybridized state).



3. Bridging NO

Nitrosyl group similar to carbonyls, can form bridge between two or three metal atoms, similar or dissimilar.

A few principles and generalizations have been derived from structural[151-157] and spectral studies[158-160] of nitrosyl complexes. A complete assignment of the factors that suggests one type of bonding over the other one, however has not been described. In order to distinguish between different types of bonding several physical methods have been used.

C.1 Infra-Red Spectral Studies

The most easily accessible and convenient technique for characterizing bonding modes of NO in transition metal complexes is IR spectroscopy. Nitrosyl complexes show a characteristic intense absorption band in the region 2000-1500 cm^{-1} due to (ν_{NO}) mode of vibration. NO stretching frequencies for the linear M-NO generally appear at higher wave number than that in the bent structure.[161] The position of (ν_{NO}) further depends on the coordination number, the oxidation state of the metal ion in the complex and its geometry. However, because of the overlap of (ν_{NO}) frequencies of linear and bent nitrosyls in 1720-1600 cm^{-1} region in some complexes, it is impossible to make a definite bonding assignment of NO.

After a careful study of a few hundreds of nitrosyl complexes, Ibers[162] has proposed a set of empirical rules correlating the positions of (ν_{NO}) with the mode of bonding in the complexes. It has been concluded that if some corrections are made in the

observed frequency of (ν_{NO}), the corrected position of (ν_{NO}) will be able to suggest the bonding modes in the nitrosyls.

After applying the corrections, the stretching frequencies of NO (ν'_{NO}) fall at least into two groups.

(a) (ν'_{NO}) below 1620–1610 cm^{-1} for complexes having bent nitrosyl ligand

(b) (ν'_{NO}) above 1620-1610 cm^{-1} for linear nitrosyl complexes.

Attempts have also been made to assign bent or linear structure on the basis of the difference between $\nu(^{15}NO)$ and $\nu'(^{14}NO)$.[163,164]

In the spectra of complexes where (ν_{NO}) appears at 1500 cm^{-1} and slightly below, nitrosyl group acts as a bridging ligand betwee the two metal centers.[165]

C.1(a) Geometry of the Metal-Nitrosyl complexes

Eight rules have been formulated by Ibers[166] for predecting the geometry of nitrosyl complexes. These are

1. Without the assistance of special ligand, first row transition metals usually do not have enough power by themselves to bend the nitrosyl ligand, second row metals often do and third row metals usually do.

2. Number and size of bulky ligands play an important role, as they usually do in the least steric hindered position. In

case only one such ligand is present, it usually occupies the non-axial position. With two such ligands present, both are usually present in the trans position, and occupy the axial sites in 'tbp' and non-axial sites in 'spy'. With three such ligands, the 'spy' geometry is usually not found, and all three would occupy the non-axial sites in tbp.

3. Strong π-acceptor ligands such as CO and NO (linear) and also σ-donor ligands with large trans influence or trans effect such as H or NO (bent) prefer not to be trans to each other in any combination, if possible.

4. Re and probably W and Mo which form strong nitrosyl multiple bonds, and prefer ligands which are good π-acceptors, retard the bending of the attached nitrosyl ligand.

5. If two bidentate ligands are present in the metal nitrosyl, the complex usually favours the tbp geometry with equatorial NO.

6. Special multidentate ligands can promote one geometry over the another, $HC(CH_2Ph_2)_3$ stabilizes the 'sp' geometry.

7. Ligands which deactivate the metal, by removing the electron density from it, thereby decreasing its reducing power, favour the tbp geometry and conversely.

8. If the integrity of nitrosyl ligand is maintained, all 20 electron systems must have bent nitrosyls. Six coordinate $16e^-$, $18e^-$ and $17e^-$ nitrosyl complexes have linear nitrosyl

group. Six coordinate, $19e^-$ systems probably have bent NO with M-N-O angle, distinctly larger than 120^o.

The nature of bonding in the transition metal nitrosyls has also been described in terms of molecular orbital theory by Manoharan and Gray[167] and by Fenske and Dekock,[168] Pierpont and Eisenberg,[169] Enemark and Feltham[29] Hoffman and his coworkers.

1.3 TRANSITION METAL THIONITROSYLS

Although the nitrosyl complexes of transition metals have created considerable interest in coordination chemistry for over a century, the chemistry of the complexes containing coordinated thionitrosyl group 'NS' is only a decade old. The first few transition metal thionitrosyl complexes were reported by Chatt and Dilworth in 1974.[170] Since then a large number of reports have appeared and they have been comprehensively reviewed recently.[24a,b] One of the reasons for the sluggishness in the development of S-N chemistry is the instability of the NS radical compared to NO radical and the non-availability of a convenient thionitrosylating agent.

A brief up to date account of the transition metal thionitrosyl chemistry which includes synthetic routes, physicochemical properties and bonding modes of the thionitrosyl group is given below.

1.3.A Thionitrosyl group

Chemistry of the thionitrosyl group including its covalent compounds and transition metal complexes has been described at length in reviews by Agarwala et al.[171] and Roesky and Pandey.[172] Detailed account of the sulphur-nitrogen chemistry was covered in two recent reviews.[24a,b]

Presence of thionitrosyl monomer NS was observed for the first time by Fowler and Bakker in 1932. The NS radical with an unpaired electron, unlike its homolog NO, polymerizes too rapidly to isolate it as a monomer in the solid, liquid or the gas phase. It has only a transient existence.[173] Analogous to NO, it can lose or gain an electron to form NS^+ or NS^-, respectively and most of its properties are similar to those of NO. The comparisons of some of the physical properties of NO and NS were given in literature.[17

A calculated electronic configuration of the ground state of NS is $5\sigma^2$, $6\sigma^2$, $7\sigma^2$, $2\pi^4$, $3\pi^1$ where the valence electrons of sulphur and nitrogen are considered. A large number of papers related to microwave spectrum of NS have appeared in the literature[174] and the excited valence states $B^2\pi$, $A^2\Delta$, $G^2\Sigma^-$, $H^2\pi$ and $I^2\Sigma^+$ have been identified in addition to the ground state $X^2\pi$.

NS is a paramagnetic molecule having a doublet $2\pi_{1/2}$ ground state with the lowest excited state, $2\pi_{3/2}$ lying about 223 cm^{-1} above the ground state level. Its ESR spectrum has been studied[175

which consists of three triplets. The g factor is consistent with the value expected for a molecule in a $2\pi_{3/2}$ state in the lowest rotational level with J = 3/2. IR spectrum of NS shows a very weak band at 1225 cm^{-1}. The vibrational frequencies of gaseous NS is given as 1204.1 cm^{-1}.[171]

Three important covalent compounds of NS are NSF, NSF_3 and NSCl. On the basis of the value of (ν_{NS}) in NSF (1372 cm^{-1}), it appears that the bond order of NS is less than in NSF_3 (1515 cm^{-1}) and greater than that in NSCl (1320 cm^{-1}). Various attempts to correlate the bond length (ν_{NS}) and the bond order of NS in order to characterize the NS bond in NSX (X = Cl, F, F_3) resulted in the following relationship between the force constant, (f_{NS}) and (ν_{NS}).[176]

$$f_{NS} = 1.45\ \nu_{NS} - 7.00$$

Thionitrosyl chloride which is a greenish yellow gas, rapidly polymerizes to a stable trimer.[177]

$$3\ NSCl \rightleftharpoons N_3S_3Cl_3$$

It is susceptible to hydrolyses in the presence of water even in traces to yield HNSO, NH_4^+, SO_3^{2-}, H^+ and Cl^- ions.[178] Thus

$$NSCl + H_2O \rightleftharpoons HNSO + HCl$$

$$HNSO + 2H_2O \rightleftharpoons NH_4^+ + SO_2^{2-} + H^+$$

1.3.B Synthetic methods

Only a few methods are available for the synthesis of metal thionitrosyl complexes. Among all the thionitrosylating reagents $N_3S_3Cl_3$ has been used with some success. A overview of different reagents and synthetic methods used is given below.

B.1 Trithiazyl trichloride, $N_3S_3Cl_3$

Treatment of $N_3S_3Cl_3$ with transition metal salts or complexes results in the formation of a variety of NS complexes. The first transition metal thionitrosyl complex was prepared using $N_3S_3Cl_3$ by Kolthammer and Legzdins in 1978.[179]

$$Na[Cr(CO)_3cp] + \frac{1}{3} N_3S_3Cl_3 \xrightarrow{THF} [Cr(CO)_2cpNS]$$

During the same time the use of $N_3S_3Cl_3$ as thionitrosylating agent was exploited by Agarwala and coworkers in the synthesis of ruthenium, osmium, cobalt thionitrosyl complexes.[20,22] Ruthenium trichloride was treated with PPh_3 or $AsPh_3$ followed by $N_3S_3Cl_3$, resulting in $[Ru(NS)Cl_3(PPh_3)_2]$ or $[Ru(NS)Cl_3(AsPh_3)_2]$ but the more reliable route starts from $[RuCl_2(PPh_3)_3]$.

$$[MCl_3(PPh_3)_3] + \frac{1}{3} N_3S_3Cl_3 \xrightarrow{THF} [M(NS)Cl_3(PPh_3)_2]$$

(M = Ru, Os)

$$[CoH\{P(OPh)_3\}_4] + N_3S_3Cl_3 \xrightarrow{THF} [Co(NS)Cl_2\{P(OPh)_3\}_2] \longrightarrow$$

$$[Co(NSO)Cl_2\{P(OPh)_3\}_2] \qquad [23]$$

The first transition metal complexes with NSCl as a ligand was reported by Dehnicke and coworkers in 1982,[180] followed by the synthesis and structural characterization of a large number of NSCl complexes. In these complexes NSCl behaves as neutral NSCl, $NSCl^-$ and $NSCl^{2-}$ etc.

$$VCl_4 + N_3S_3Cl_3 \longrightarrow [VCl_3(NSCl)_2]_2 \qquad [181]$$

$$ReCl_5 + N_3S_3Cl_3 \xrightarrow{POCl_3} [ReCl_4(NSCl)(POCl_3)] \qquad [182]$$

and

$$[ReCl_3(NSCl)_2(POCl_3)]$$

$$MoCl_5 + 2/3\ N_3S_3Cl_3 \longrightarrow [MoCl_4(NSCl)] \qquad [183]$$

$$MCl_6 + 2/3\ N_3S_3Cl_3 \longrightarrow [MCl_4(NSCl)_2]_2 \qquad [184]$$

(M = Mo or W)

$$MCl_5 + 1/3\ N_3S_3Cl_3 \xrightarrow{CCl_4} [M(NSCl)Cl_5] \qquad [185]$$

(M = Nb or Ta)

$$OsCl_5 + N_3S_3Cl_3 \longrightarrow [OsCl_4(NSCl)_2] \xrightarrow[CH_2Cl_2]{AsPh_4Cl} [AsPh_4][OsCl_4(NS)_2Cl] \qquad [186]$$

$$[AsPh_4][OsCl_4(NS)_2Cl] \xrightarrow[CH_2Cl_2]{GaCl_3} [OsCl_4(NS)_2]$$

$$PPh_4[OsCl_4(NO)]_2 + N_3S_3Cl_3 \xrightarrow{CH_2Cl_2} PPh_4[OsCl_4(NO)(NSCl)] \qquad [187]$$

Some of the complexes prepared from $N_3S_3Cl_3$ and metal chlorides do not have NS^+ or NSCl as ligands. They contain ring compounds of sulphur-nitrogen as ligands.

$$MoNCl_3 + N_3S_3Cl_3 \longrightarrow [MoCl_3(N_3S_2)]_2 \qquad [188]$$

$$ZrCl_4 + N_3S_3Cl_3 \longrightarrow (S_3N_3Cl_2)_2[Zr_2Cl_{10}] \qquad [189]$$

$$TiCl_4 + N_3S_3Cl_3 \longrightarrow [TiCl_4(N_2S_2)] \qquad [190]$$

$$MoCl_5 + N_3S_3Cl_3 \xrightarrow{CH_2Cl_2} (\mu\text{-}S_2N_2)[MoCl_4(NSCl)]_2 \qquad [191]$$

B.2 Thiazyl fluoride

The chemistry of NSF and NSF_3 has been surveyed recently by Glemser and Mews. The combination of moisture senstivity with thermal instability makes them difficult to be handled. However, thiazyl fluoride can be stabilized by coordination to transition metal ions. These are conveniently prepared in liquid SO_2.

$$M(SO_2)[AsF_6]_2 + 6\ NSF \xrightarrow[-2SO_2]{-20^{\circ}C} [M(NSF)_6AsF_6]_2 + 2\ SO_2 \qquad [192]$$

(M = Co or Ni)

Introduction of NSF as a ligand into cationic carbonyl metal compounds is also achieved via SO_2 complexes.

$$[Re(CO)_5SO_2][AsF_6] + NSF \xrightarrow[SO_2]{-30^{\circ}C} [Re(CO)_5NSF][AsF_6] + SO_2$$

NSF_3 is thermally more stable than NSF. The synthetic approach to transition metal complexes of NSF_3 is similar to that described above for NSF.

$$[M(SO_2)][AsF_6]_2 + 4\ NSF_3 \longrightarrow [M(NSF)_4][AsF_6]_2 + 2\ SO_2 \qquad [193]$$

(M = Mn, Fe, Co, Ni or Cu)

$$[M(CO)_5SO_2][AsF_6] + NSF_3 \xrightarrow{SO_2} [M(CO)_5NSF_3][AsF_6] \qquad [194]$$

(M = Mn or Re)

B.3 NS^+X^-

Only a few thionitrosyl complexes have been synthesized using NS^+ salts as thionitrosylating agents.[195] Mews and Liu[196] have exploited their use for the synthesis of metal thionitrosyls by reacting them with metal ions or their complexes.

$$[Re(CO)_5Br] + NS^+SbF_6^- \longrightarrow [Re(CO)_5NS][SbF_6]_2$$

$$[(C_6H_6)Cr(CO)_3] + NS^+PF_6^- \xrightarrow{MeCN} [Cr(NS)(MeCN)_5][PF_6]_2$$

$$[Re(CO)_5(SO_2)][AsF_6] + NS^+PF_6^- \longrightarrow [Re(CO)_5NS][AsF_6]_2 + SO_2$$

B.4 Elemental Sulphur

Sulphur abstraction from elemental sulphur by a nitrido complex was the strategy used by Chatt and coworkers to prepare

NS complexes. They have synthesized the thionitrosyl of Mo, Ru, Os.

$$[MoN(S_2CNR_2)_3] + S_8 \longrightarrow [Mo(NS)(S_2CNR_2)_3] \qquad [197]$$

(R_2 = 2 Me, 2 Et or $(CH_2)_4$]

B.5 Disulphur dichloride, S_2Cl_2

The preparative route through S_2Cl_2 is similar to that of S_8. It was first used for the synthesis of Re and Os thionitrosyls[198] and later extended for the preparation of Tc(I) and Tc(II) thionitrosyls.[199]

$$[ReNCl_2(PRPh_2)_2 + S_2Cl_2 \longrightarrow [Re(NS)Cl_3(PRPh_2)_2]$$

$$[OSNX_3L_2] + S_2Cl_2 \longrightarrow [Os(NS)Cl_3L_2]$$

(X = Cl; L = $2PMe_2Ph$, Bipy, $2AsPh_3$)

$$[L_3TcCl_2N] + S_2Cl_2 \longrightarrow [L_3TcCl_x(NS)]$$

(L = $PhMe_2P$; X = 2,3)

Both the above methods (S_8, S_2Cl_2) though yield sufficient number of complexes can not be generalized.

B.6 S-N Compounds

Several S-N compounds have also been used though less frequently than $N_3S_3Cl_3$ for the synthesis of M-NSCl complexes. Thus,

$$WCl_6 + S_3N_2Cl_2 \xrightarrow{CCl_4} [N(SCl)_2][WCl_5NSCl] \quad [200]$$

$$ReCl_5 + S_3N_2Cl \xrightarrow{CH_2Cl_2} [ReCl_3(NSCl)_2]_2 \quad [201]$$

Recently the first example of the preparation of transition metal thionitrosyl complexes using S_4N_4 as thionitrosylating agent has been reported.

$$Re_2Cl_{10} + S_4N_4 \xrightarrow[CH_2Cl_2]{Ph_4AsCl} [Ph_4As][Re(NS)Cl_5] \quad [202]$$

1.3.c Properties of Thionitrosyl Complexes

The ligand NS might be expected to have bonding properties similar to those of NO. Analogous to nitrosyl complexes the most readily accessible and sensitive technique for identifying metal thionitrosyls is IR spectroscopy. A variety of other physical technique like NMR, X-ray spectroscopy, helped in confirming the structure and bonding in the metal thionitrosyl complexes.[203,182,202]

C.1 Theoretical Studies

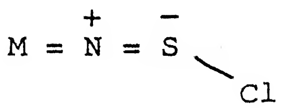
It has been shown previously that NS is a better σ-donor and π-acceptor than NO. Physical measurements have supported the conclusion that NS binds more strongly to an electron rich metal than does NO. An investigation of the electronic structure of $[(\eta^5\text{-}C_5H_5)Cr(CO)_2NS]$ by photoelectron spectroscopy[204] and

theoretical calculations has been reported by Lichtenberger and Fenske.[205] Their studies confirm the early predictions of NS being a better σ-donor than NO which was based on molecular orbital calculations.

C.2 IR

The NS stretching frequency in the linear M-NS complexes generally appears in the range between 1370–1065 cm^{-1}.[179,198,20,206]

The IR spectra of M-NSCl complexes have been discussed in detail by Dehnicke and coworkers. The bonding in M-NSCl complexes can be described in terms of resonance structure 1 and 2, complexes in which 1 is dominant show a characteristic strong band at



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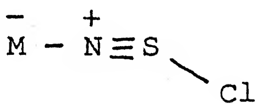

2

1000–900 cm^{-1},[182,191,207] which has been assigned to ν_{as}(MNS). The IR spectra of compounds with a larger contribution from resonance from 2 show ($\nu_{N\equiv S}$) bands at 1360–1290 cm^{-1}.[201,208,181]

C.3 NMR Studies

The ^{1}H NMR spectrum of $[(\eta^5\text{-}C_5H_5)Cr(CO)_2(NS)]$ consist of a single sharp peak due to protons of C_5H_5. It appears at a slightly

lower field than the corresponding absorption in the spectra of nitrosyl analogs.

^{13}C and ^{14}N NMR data have been reported for three pairs of metal nitrosyl/thionitrosyl compounds.[209] Only small changes in the ^{13}C NMR chemical shift of CO ligands are observed. However the ^{14}N chemical shifts increase by as much as 49 ppm for an NS compared to that of analogous NO complex. The deshielding of ^{14}N nuclei has been attributed to a decrease in the energies of the low lying excited states for the M-N-S complexes.

C.4 Mass Spectral data

In order to gain further insight into the bonding of Cr–NX, Legzdins, et al. investigated the low resolution mass spectra of the $[Mo(NS)(S_2CNR_2)_3]$ (R_2 = Me_2, Et_2, $(CH_2)_4$] which show peaks attributable to the parent ions.

C.5 X–Ray

Although more than 70 metal–thionitrosyl complexes have been described, X–ray structural data are available for only six complexes.[24]

The crystal structure of $[Cr(CO)_2cp(NS)]$ reveals the normal piano stool structure with a Cr–N–S angle of 176.8^{o} and an NS bond length of 1.55 A.

The linear arrangement of the NS group has been assigned by X-ray for $[M(NS)Cl_3(PPh_3)_2]$ (M = Os).[206] The structure of $[Mo(NS)(S_2CNMe_2)_3]$ is pentagonal bipyramidal with a linear apical NS group.

X-ray structural data for M-NSCl complexes have been given in the literature.[24]

In the case of molybdenum complexes, the NSCl group is thought to be bent with the M-N bond having considerable double bond character.

In the case of $[ReCl_4(NSCl)][AsPh_4]_2$ the M-N distance (1.78 A^o) and NS distance (1.53 A^o) suggest an M=N=S structure with octahedral geometry.

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Chapter - II

Reactions of NOX ($X = Cl^-$, Br^-, or Br_3^-) with Cyclopentadienyl Ruthenium Complexes

2.1 Introduction

The structure, the bonding and the reactivity of transition metal nitrosyls have been a provocative subject for the past many years.[1-6] NOX ($X = Cl^-$, Br^-, or Br_3^-) have previously been used to introduce nitrosyl group into organo-metallic complexes.[7-11] It generally reacts by simple oxidative addition mechanism. Some work related to this field has already been carried out in the past by us.[12,13]

In this chapter the results of the reactions of NOX ($X = Cl^-$, Br^- or Br_3^-) with η^5-cyclopentadienyl ruthenium complexes of type $[Ru(\eta^5-C_5H_5)(EPh_3)(L-L)]^+X^-$ or $[Ru(\eta^5-C_5H_5)X(EPh_3)L]$ (where E = As, Sb; L-L = 2,2'-Bipyridine, 1,10-Phenanthroline; L = Pyridine, γ-Picoline, $SbPh_3$, $AsPh_3$, PPh_3 and $X = Cl^-$, Br^-, I^-, CN^-, NCS^-) have been

described. The reaction products are characterized by various physicochemical analyses.

2.2 Experimental

All chemicals used were of Analar grade. Solvents were dried and distilled before use. Nitrosyl chloride, nitrosyl bromide and nitrosyltribromide were prepared according to the method described in the literature.[14-16] The complexes $[Ru(\eta^5-C_5H_5)X(EPh_3)_2]$, $[Ru(\eta^5-C_5H_5)(EPh_3)L-L]^+X^-$ and $[Ru(\eta^5-C_5H_5)(EPh_3)LX]$ (where E = P, As, Sb) were prepared by the literature methods.[17-19]

A. Preparation of Complexes

I. Reactions with Nitrosyl chloride (NOCl)

(1) Reactions of $[Ru(\eta^5-C_5H_5)X(EPh_3)_2]$ (E = As, Sb; X = Cl^-, Br^-, I^-)

30 ml of a solution of the complex $[Ru(\eta^5-C_5H_5)X(EPh_3)_2]$ (0.1 mmol) in methanol and dichloromethane mixture (2:1, v/v) was mixed with a saturated dichloromethane solution of NOCl (5 ml). The resulting solution was refluxed for about an hour, whereby golden yellow crystals of $[Ru(NO)Cl_3(EPh_3)_2]$ were formed. These were separated by filtration, washed with methanol, ether and dried under vacuum. Addition of a small amount of EPh_3 during the reaction, enhanced the yield of the reaction products (yield, ca 70%).

(2) Reactions of [Ru(η^5-C_5H_5)X(EPh_3)$_2$] (E = As, Sb; X = CN^-, NCS^-)

A saturated solution of NOCl in dichloromethane (5 ml) was added very slowly to a solution of [Ru(η^5-C_5H_5)X(EPh_3)$_2$] (0.12 mmol) in a mixture of methanol (25 ml) and dichloromethane (10 ml). The reaction mixture was heated under reflux for about two hours whereupon an oily product was formed as a separate layer. It was separated and from the oily product a pure crystalline solid was obtained, though with difficulty, after repeated trials of dissolution of the oil in CH_2Cl_2 with a subsequent addition of light petroleum ether to it. It gave a brown solid product which was filtered, washed with hexane and dried in vacuo. The product was analysed for [Ru(NO)XCl_2(EPh_3)$_2$] (X = CN^-, NCS^-).

If a small amount of EPh_3 was added in the reaction mixture during refluxing, formation of [Ru(NO)Cl_3(EPh_3)$_2$] had taken place.

(3) Reactions of [Ru(η^5-C_5H_5)(EPh_3)L-L]$^+$$X^-$ (L-L = 2,2'-bipy, 1,10-phen; X = Cl^-, Br^-, I^-, CN^-, NCS^-)

10 ml of a saturated solution of NOCl was added to 45 ml solution of [Ru(η^5-C_5H_5)(EPh_3)L-L]$^+$$X^-$(0.2 mmol) in MeOH:$CH_2Cl_2$ (2:1, v/v) mixture and the resulting solution was refluxed for about an hour whereupon the colour of the solution turned to green. It was concentrated to about 10 ml. After addition of petroleum ether (60-80°) to the concentrate, the green shining crystals were

separated. These were filtered, recrystallised from CH_2Cl_2/pet. ether (40–60^o), washed several times with petroleum ether and dried under vacuum. The product analysed for $[Ru(NO)Cl_2(EPh_3)-(L-L)]^+Cl^-$.

(4) <u>Reactions of $[Ru(\eta^5-C_5H_5)(EPh_3)LX]$ (E = As; L = py, γ-pic; X = Cl^-, Br^-, I^-, CN^-, NCS^-)</u>

To a chloroform solution (20 ml) of $[Ru(\eta^5-C_5H_5)X(AsPh_3)L]$ (0.1 mmol) a saturated solution of NOCl in CH_2Cl_2 (5 ml) was slowly added, followed by the addition of 20 ml of methanol. The reaction mixture was refluxed for two hours. On concentrating the resulting solution on a water-bath, the orange coloured micro-crystals appeared in the solution which were separated by filtration, washed with methanol, ether and dried under vacuum.

(5) <u>Reactions of $[Ru(\eta^5-C_5H_5)(SbPh_3)LX]$ (L = py, γ-pic; X = Cl^-, Br^-, I^-, CN^-, NCS^-)</u>

A saturated solution of NOCl (CH_2Cl_2, 10 ml) was added to a solution of $[Ru(\eta^5-C_5H_5)X(SbPh_3)L]$ (0.12 mmol) in a mixture of chloroform (15 ml) and methanol (25 ml). The resulting solution was refluxed for an hour and the resulting solution was concentrated to near dryness. All attempts to separate a solid product by adding excess of hexane failed. It always yielded an oily mass. Repeated attempts using other solvents to purify the product could

not separate the solid compound. However, the addition of a small amount of $SbPh_3$ initially to the reaction mixturesyielded pure $[Ru(NO)Cl_3(SbPh_3)L]$ in low yield (yield, ca. 40).

(6) Reactions of $[Ru(\eta^5-C_5H_5)X(AsPh_3)(PPh_3)]$ ($X = Cl^-, Br^-, I^-, CN^-, NCS^-$)

The reactions were carried out by a method similar to the one described in (1), except that $[Ru(\eta^5-C_5H_5)X(AsPh_3)(PPh_3)]$ was taken in place of $[Ru(\eta^5-C_5H_5)X(EPh_3)_2]$. Dark orange crystals of $[Ru(NO)Cl_3(AsPh_3)(PPh_3)]$ were separated out, which were washed as described in (1).

In case of CN complexes repeated attempts to recrystallise the oil afforded $[Ru(NO)CNCl_2(AsPh_3)(PPh_3)]$. Addition of $AsPh_3$ or PPh_3 in the reaction mixture led to the formation of $[Ru(NO)Cl_3(AsPh_3)_2]$ or $[Ru(NO)Cl_3(PPh_3)_2]$.

II. Reactions with Nitrosyl Bromide (NOBr)

(7) Reactions of $[Ru(\eta^5-C_5H_5)X(EPh_3)_2$ (E = As, Sb; $X = Cl^-, Br^-, I^-, CN^-, NCS^-$)

20 ml of the dichloromethane solution of $[Ru(\eta^5-C_5H_5)X(EPh_3)_2]$ (0.15 mmol) was mixed with 5 ml of a saturated solution of NOBr in CH_2Cl_2. After further addition of 25 ml of methanol to the solution, the reaction mixture was refluxed for about 30 minutes.

The resulting orange solution was concentrated on water bath whereupon yellowish-orange shining microcrystals were formed, which were separated by centrifugation, washed with methanol, ether and dried under vacuum.

In the case of $[Ru(\eta^5-C_5H_5)Br(EPh_3)_2]$, orange crystals of $[Ru(NO)Br_3(EPh_3)_2]$ were obtained.

(8) Reactions of $[Ru(\eta^5-C_5H_5)(EPh_3)(L-L)]^+X^-$ (E = As, Sb; L-L = 2,2'-bipy, 1,10-phen; X = Cl^-, Br^-, I^-, CN^-, NCS^-)

A saturated dichloromethane solution of NOBr (15 ml) was slowly added to an orange coloured solution of $[Ru(\eta^5-C_5H_5)(EPh_3)$-L-L]X (0.12 mmol) in a mixture of 15 ml of dichloromethane and 40 ml of methanol. The resulting solution was refluxed for 2 hours. The resulting green solution was concentrated to about 10 ml and addition of excess of hexane to it yielded green microcrystals. These were separated by filtration, washed with hexane and dried under vacuum. The green product thus obtained was recrystallised several times with methanol/ether.

(9) Reactions of $[Ru(\eta^5-C_5H_5)X(EPh_3)L]$ (E = As; L = py, γ-pic; X = Cl^-, Br^-, I^-, CN^-, NCS^-)

The reactions were carried out by a method similar to that given in (4), except that $[Ru(\eta^5-C_5H_5)X(EPh_3)L]$ (0.15 mmol) was

taken in the place of [Ru(η^5-C_5H_5)X(EPh_3)$_2$]. The yellow coloured complex [Ru(NO)ClBr_2(EPh_3)L] or [Ru(NO)Br_3(EPh_3)L] that was obtained, separated by centrifugation, washed with methanol, ether and finally dried in vacuo.

(10) Reactions of [Ru(η^5-C_5H_5)X(EPh_3)L] (E = Sb; L = py, γ-pic; X = Cl^-, Br^-)

A saturated dichloromethane solution of NOBr (5 ml) was slowly added to the yellow coloured solution of [Ru(η^5-C_5H_5)-X(EPh_3)L] (0.2 mmol) in a mixture of 20 ml of chloroform and 30 ml of methanol. The reaction mixture was refluxed for 30 minutes. A little amount of $SbPh_3$ was added to the reaction mixture. It was further refluxed for a period of another 30 minutes. On cooling the reaction mixture, yellow crystals were separated out from the solution. They were filtered, washed with methanol, diethyl ether and dried in vacuo. It was analysed for [Ru(NO)X_3-(EPh_3)L].

(11) Reactions of [Ru(η^5-C_5H_5)X($AsPh_3$)(PPh_3)] (X = Cl^-, Br^-, I^-, CN^-, NCS^-)

The method for these reactions was similar to that given in (7), except that [Ru(η^5-C_5H_5)X($AsPh_3$)(PPh_3)] was used in place of [Ru(η^5-C_5H_5)X(EPh_3)$_2$]. The orange coloured product was separated, purified and dried under vacuum.

III. Reactions with $NOBr_3$

(12) Reactions with $[Ru(\eta^5-C_5H_5)X(EPh_3)_2]$ (E = As; X = Cl^-, Br^-, I^-, CN^-, NCS^-)

A saturated dichloromethane solution of $NOBr_3$ (5 ml) was added slowly with stirring to a solution of $[Ru(\eta^5-C_5H_5)X(EPh_3)_2]$ (0.12 mmol) in a mixture of methanol and dichloromethane (2:1, v/v). The solution was refluxed for about an hour whereupon shining orange crystals of $[Ru(NO)Br_3(EPh_3)_2]$ were separated out. The product was filtered, washed with methanol, ether and finally dried *in vacuo*.

(13) Reactions of $[Ru(\eta^5-C_5H_5)X(EPh_3)_2]$ (E = Sb; X = Cl^-, Br^-, CN^-)

$[Ru(\eta^5-C_5H_5)X(EPh_3)_2]$ (0.12 mmol) in a mixture of 20 ml of CH_2Cl_2 and 40 ml of methanol, was added to a saturated CH_2Cl_2 solution of $NOBr_3$ (5 ml), and the reaction mixture was refluxed for one hour. Addition of a few crystals (*ca.* 0.05 g) of $SbPh_3$ to the solution and heating it further under reflux for 30 minutes, afforded orange crystals of $[Ru(NO)Br_3(EPh_3)_2]$ or brown crystals of $[Ru(NO)(CN)Br_2(EPh_3)_2]$, which were filtered, washed with methanol, ether and finally vacuum dried.

(14) Reactions of $[Ru(\eta^5-C_5H_5)(EPh_3)L-L]^+X^-$ (E = As; L-L = 2,2'-bipy, 1,10-phen; X = Cl^-, Br^-, I^-, CN^-, NCS^-)

40 ml of a solution of complexes $[Ru(\eta^5-C_5H_5)(EPh_3)L-L]^+X^-$ (0.2 mmol) in methanol and dichloromethane mixture (2:1, v/v) was mixed with a saturated dichloromethane solution of $NOBr_3$ (5 ml). The resulting mixture was refluxed for about an hour, whereupon black microcrystals of $[RuBr_3(EPh_3)L-L]$ were obtained. The filtrate was subsequently concentrated to about 10 ml, followed by addition of excess petroleum ether (60–80°) whereupon green shining crystals were separated. These were filtered, recrystallised from CH_2Cl_2/ pet. ether (40–60°), washed several times with petroleum ether and dried.

(15) Reactions of $[Ru(\eta^5-C_5H_5)(EPh_3)L-L]^+X^-$ (E = Sb; X = Cl, Br; L-L = 2,2'-bipy, 1,10-phen)

The reaction was carried out by a procedure similar to the one described in (14).

(16) Reactions of $[Ru(\eta^5-C_5H_5)(EPh_3)LX]$ (E = As; L = py, γ-pic; X = Cl^-, Br^-, I^-, CN^-, NCS^-)

A preparative method similar to that given in (4) was carried out, yielded yellow crystals, which were filtered and washed with methanol, ether and dried.

(17) Reactions of [Ru(η^5-C_5H_5)X($AsPh_3$)(PPh_3)] (X = Cl^-, Br^-, I^-, CN^-, NCS^-)

The reaction was carried out by a procedure similar to the one described in (12), except that [Ru(η^5-C_5H_5)X($AsPh_3$)(PPh_3)] was used in place of [Ru(η^5-C_5H_5)X(EPh_3)$_2$]. The reactions yielded microcrystals of [Ru(NO)Br_3($AsPh_3$)(PPh_3)] which were separated by centrifugation, washed with methanol, ether and finally dried under vacuum.

(B) Analyses and physico chemical measurements

Carbon, hydrogen and nitrogen were analysed by the Micro-analytical Laboratory of the Indian Institute of Technology, Kanpur, India. Halogens were analysed by a standard method reported elsewhere.[20] Melting points were determined on a Fischer-Johns melting point apparatus and are uncorrected. Electronic absorption spectra of the complexes were recorded in dichloromethane on the Cary 17-D spectrometer. The ir spectra (4000-200 cm^{-1}) were recorded on the Perkin Elmer 580 spectrophotometer. Samples were prepared as KBr pallets. ^1H nmr were recorded on Bruker WP 80 spectrometer.

2.3 Results and Discussion

The preparations of the ruthenium nitrosyl compounds were carried out according to the general reaction,

$$[M(\eta^5\text{-}C_5H_5)X(EPh_3)_2] \xrightarrow{NOX} [M(NO)X_3(EPh_3)_2]$$

(E = P, As, Sb)
(M=Ru)

The analytical data of the compounds are given in Table 2.1. They are readily soluble in halo solvents and practically insoluble in alcohols (except cationic compounds, which were soluble in alcohols) and non-polar solvents.

The reactions of (triphenylphosphine) cyclopentadienyl ruthenium(II) complexes yielded nitrosyl complexes in a very good yield. In general, the reactions were very neat, and led to the formation of very pure microcrystalline products.[12,13] However, the reactions of triphenyarsine complexes, took relatively longe refluxing time for the formation of nitrosyl complexes in a rather poorer yield. Interestingly in some cases addition of $AsPh_3$, duri the course of reaction enhanced the yield of the reaction product. T reactions of triphenylstibine complexes yielded an oily product in most of the cases and the desired product was obtained,only after the addition of an extra amount of $SbPh_3$ and that too, in low yield.

Attempts to extend the series of reactions to include cyanato and thiocyanato complexes, were not successful because the reaction products invariably appeared as oils in all the cases. All attempts to separate the crystalline product from the oil failed. However, in a few cases an impure brown solid product was isolated whose spectrum showed bands due to CN^- or NCS^- group around 2000 or 2100 cm^{-1} respectively. As stated in the experimental section, the addition of a few milligrams of $AsPh_3$ or $SbPh_3$ in the reaction mixture led to the separation of a product in which CN^- or NCS^- had been substituted by Br^- or Cl^-.

The thiocyanato complexes of triphenylarsine and triphenylstibine gave a brown product contaminated with some black product containing SO_4^{2-} ions. SO_4^{2-} ions were also detected in the product obtained after drying the filtrate. Formation of sulfate ions during the reaction of thiocyanato complexes was not unexpected. Generally the NCS^- ion is very susceptible to oxidation to SO_4^{2-} or SO_3^{2-} by an oxidizing agent. NOX, being a powerful oxidizing agent, might have oxidized SCN^- to SO_4^{2-}. The presence of SO_4^{2-} was detected by chemical analyses and the ir spectra. The characteristic absorption bands of sulfato group[21] besides those of other coligands appeared at 1200 cm^{-1}, 1050 cm^{-1}, 850 cm^{-1}, 600 cm^{-1}. The addition of $AsPh_3$ or $SbPh_3$ to the reaction mixture, however led to the formation of a microcrystalline product $[Ru(NO)X_3(EPh_3)_2]$.

From the results of these reactions it is suggested that the stability of the cyclopentadienyl complexes decrease in the series $PPh_3 > AsPh_3 > SbPh_3$ which may be due to steric effects.[22] The addition of NOX to the solution of these complexes initially starts dissociating them, followed by oxidation of the liberated PPh_3, $AsPh_3$ or $SbPh_3$. At the same time, a parallel nitrosylation reaction with the formation of $[Ru(NO)X_3(EPh_3)_2]$ also ensues. Possibly, the rate of oxidation of EPh_3 molecule increases in the order $PPh_3 < AsPh_3 < SbPh_3$ which will result in the decrease of concentration of EPh_3 as $P > As > Sb$. Thus nitrosyl complexes of stibine will be formed in the lowest yield because of the lowest concentration of $SbPh_3$ along with other oxidation products yielding an overall oily mixture, that of PPh_3 will be in good yield and that of $AsPh_3$, in moderate yield. By the addition of extra $AsPh_3$ or $SbPh_3$ to the reaction medium, rate of nitrosylation reaction possibly increases assisting the formation of insoluble or sparingly soluble nitrosyls in good yields.

The failure to synthesize thiocyanato and cyanato derivatives of the nitrosyl complexes may be due to (1) very low concentration of SCN^- or CN^- ions in the reaction mixture in comparison to that of Cl^- or Br^- ions and (2) very fast oxidation of SCN^- ion to SO_4^{2-} by NOX. The oxidation of SCN^- is evident from the presence of SO_4^{2-} in the reaction product. CN^- ion is also susceptible to oxidation under the reaction conditions.[23]

The cationic nature of the complexes has been confirmed (a) by ion exchange reactions using cationic and anionic exchangers (Dowex 50 W-XB and Dowex 1-XB) and (b) by synthesizing salts of the cations with a number of anions like BF_4^-, BPh_4^-, etc.

IR Spectra

The ir spectra of the ruthenium complexes showed an intense absorption band in the region 1880-1840 cm^{-1} which is characteristic of a terminal nitrosyl group. The positions of $\nu_{N\equiv O}$ stretching frequencies of the derivatives containing the same halogen (e.g. chloroderivatives) decrease with the variation of ligand EPh_3 (E = P $>$ As $>$ Sb)as reported earlier.[24] This may principally be attributed to the inductive effect and the π-acceptor properties of the ligands (π-acceptor properties decrease in the order($PPh_3 >$ $AsPh_3 >$ $SbPh_3$).

In the series of phosphine[5,6] and arsine derivatives, the shift in the position of ($\nu_{N\equiv O}$) decrease in order Cl $>$ Br which could be attributed to the increasing polarizability of halogens accompained by an increase in electron density on metal atom. It was also reported[25] that the neutral ligand EPh_3 causes variation in the position of ($\nu_{N\equiv O}$), and as in the case of halides, the higher frequencies are found with ligands which have greater electron attracting properties.

In the stibine series, the positions of (ν_{NO}) increase in the order Br$>$ Cl. It was suggested that triphenylstibine, which is relatively a softer ligand, further decreases the weak 'b' character of the borderline Ru(II) atom. Consequently there is a slight tendency towards mutual stabilization by the ligands. The ligand $SbPh_3$ transfers so much negative charge to the metal that the other ligands (halogens) must be sufficiently electronegative to compensate this charge. The most stable situation occurs when $SbPh_3$ and Cl^- are partners. It, thus, suggests a reason of the difficulty in the formation of $[Ru(NO)Br_3(SbPh_3)_2]$ as observed by us. Though it is obtained, but in a very low yield.

The positions of (ν_{NO}) in the pyridine and γ-picoline derivatives were about the same as those of the complexes $[Ru(NO)X_3(EPh_3)E'Ph_3)]$ (E = P, As, Sb; E' = As, Sb). This is because of the order in the ability of the additional ligands to accept metal dπ electrons $[PPh_3 > C_5H_5N >$ arylamine $> AsPh_3 > SbPh_3]$.[26]

The positions of (ν_{NO}) in the spectra of nitrosyl cationic complexes containing 2,2'-bipyridine,1,10-phenanthroline as one of the coligands, showed a high energy shift (1880-1875 cm^{-1}). This shift could be due to the electron deficiency on metal resulting in the less back donation of the π-electrons from metal to NO π^* orbital.

All the complexes show a band around 600 cm^{-1} which may be assigned to the Ru-N-O stretching vibration. The spectra also exhibit two bands due to (ν_{Ru-X}) in the region around 320-280 cm^{-1}. One of the two bands is relatively stronger than the other.

The presence of other coligands like EPh_3 (E = P, As, Sb), pyridine, γ-picoline, 2,2'-Bipyridine, 1,10-phenanthroline in the spectra of all the complexes have been confirmed by the presence of their characteristic ir frequencies.[27-30] The medium intense band in the 850 cm^{-1} region, was not observed supporting the absence of η^5-C_5H_5 moiety in the coordination sphere.

Electronic Spectra

All the complexes showed an absorption band in the visible region around 460-430 nm. They are assigned to charge transfer bands (MLTC) attributable to $4d \rightarrow \pi^*$ transitions. They give little stereochemical information except indicating that the variation of the ligand is not sufficient to change the stereochemistry fundamentally. The spectra of all the complexes containing different ligand (triphenylphosphine, triphenylarsine and triphenylstibine), exhibited a rather broad envelope in the above region, so it became very difficult to explain the difference in the spectra of the complexes containing different ligands. But it was observed in a few cases that value of λ_{max} decreases in the order $PPh_3 \approx AsPh_3 < SbPh_3$ respectively and the ϵ value was

approximately same as reported earlier.[31] It could also be possible that the coincidence of the similar absorption maxima in the spectra of these complexes is due to the fortuitous balancing of various factors. By taking into account the large number of donor groups which are capable of creating a stronger field around the metal ion, variation in its position in visible region of Cl, Br, CN, NCS complexes, in accordance with the ligand positions in the spectrochemical series, was not regular for obtaining certain results.

In additon, because of the presence of a number of π-acceptor ligands like arsine, stibine, pyridine, γ-picoline, 2,2'-bipyridine, 1,10-phenanthroline, NO, a number of $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transition bands were present in the UV region exhibiting a complicated structure of the band.

NMR

^1H NMR spectra of the complexes were studied to substantiate the presence or the absence of the coligand molecules. All the spectra showed more or less identical features, a poorly resolved broad multiplet of the protons of the phenyl and heterocyclic group in the region around (δ 7.0–8.5). In the case of picoline an additional band around (δ 2.0) was present due to methyl protons. The evidence bearing the absence of cyclopentadienyl group has been further obtained by the absence of a band in δ 4–5 region.

In conclusion, we wish to point out that NOX provide an efficient source for nitrosylation for various η^5-cyclopentadienyl ruthenium(II) complexes. In all cases except a few, the nitrosyl products were isolated without difficulty with the loss of η^5-cyclopentadienyl moiety in coordination sphere during nitrosylation.

Table 2.1. Reactions of $[Ru(\eta^5-C_5H_5)(EPh_3)LX]$ with NOX. Characteristic Data of Complexes

No.	Parent Compd $[Ru(\eta^5-C_5H_5)(EPh_3)LX]$ LIGAND L	X	NOX (X=Cl, Br, Br3) X	Product M.P. (^oC), colour	Microanalytical data Analyses, found(calcd)% C	H	N	X	IR bands (cm^{-1})	λ_{max} (nm) CH_2Cl_2 solvent
1	2	3	4	5	6	7	8	9	10	11
	E = As									
1.	$AsPh_3$	Cl	Cl	$[Ru(NO)Cl_3(AsPh_3)_2]$ O >260	49.9 (50.8)	3.7 (3.5)	1.5 (1.6)	12.8 (12.4)	1860	430,353,310, 280
2.	Py	Cl,I	Cl	$[Ru(NO)Cl_3(AsPh_3)(Py)]$ YB 225	45.0 (44.3)	3.8 (3.2)	4.4 (4.5)	17.9 (17.0)	1860	435,390,350, 280,268
3.	4-Pic	Cl,I	Cl	$[Ru(NO)Cl_3(AsPh_3)$-(γ-Pic)] YB 220	45.8 (45.2)	4.0 (3.6)	4.7 (4.3)	17.2 (16.6)	1860	430,390,350, 280,260
* 4.	2,2'-Bipy	Cl,I	Cl	$[Ru(NO)Cl_2(AsPh_3)$-(Bipy)$]^+Cl^-$ Y 180	48.6 (48.0)	4.0 (3.2)	6.2 (6.0)	15.8 (15.1)	1880	430,390,285
	1,10-Phen	Cl,I	Cl	$[Ru(NO)Cl_2(AsPh_3)$-(Phen)$]^+Cl^-$ Y 170	48.9 (49.7)	4.2 (3.1)	5.6 (5.8)	15.2 (14.6)	1880	440,345,300, 275
	$AsPh_3$	Cl	Br	$[Ru(NO)Br_2Cl(AsPh_3)_2]$ B >260	45.2 (46.0)	3.2 (3.1)	1.8 (1.4)	19.2 (20.8)	1850	430,350,310, 270
	Py	Cl	Br	$[Ru(NO)Br_2Cl(AsPh_3)(Py)]$ YO 240	39.2 (38.7)	3.6 (2.8)	4.8 (3.9)	28.2 (27.5)	1850	430,350,280

...contd.

Table 2.1(contd.)

1	2	3	4	5	6	7	8	9	10	11
8.	4-Pic	Cl	Br	[Ru(NO)Br_2Cl($AsPh_3$)(γ-Pic)] YB 235	38.5 (39.6)	4.0 (3.1)	4.6 (3.8)	27.5 (26.9)	1850	
* 9.	2,2'-Bipy	Cl	Br	$[Ru(NO)BrCl(AsPh_3)Bipy]^+Br^-$ G 190	41.8 (42.5)	3.2 (2.9)	5.4 (5.3)	25.2 (24.8)	1880	425,360, 300,250
* 10.	1,10-Phen	Cl	Br	$[Ru(NO)BrCl(AsPh_3)(OPhen)]^+Br^-$ G 185	43.6 (44.2)	3.4 (2.8)	4.8 (5.1)	24.6 (24.1)	1880	420,300, 260,210
11.	$AsPh_3$	Br	Cl	$[Ru(NO)BrCl_2(AsPh_3)_2]$ B >260	48.8 (48.3)	3.8 (3.3)	1.6 (1.5)	17.0 (16.8)	1860	430,350, 300,285
12.	Py	Br	Cl	$[Ru(NO)BrCl_2(AsPh_3)(Py)]$ YO 226	42.1 (41.3)	3.2 (2.9)	4.8 (4.1)	21.8 (22.6)	1860	430,350, 280,260
13.	4-Pic	Br	Cl	$[Ru(NO)BrCl_2(AsPh_3)(Pic)]$ YO 220	42.8 (42.2)	3.8 (3.3)	4.8 (4.1)	22.6 (22.1)	1850	430,350, 275,260
* 14.	2,2'-Bipy	Br	Cl	$[Ru(NO)Cl_2(AsPh_3)(Bipy)]^+Cl^-$ G 180	49.2 (48.0)	3.8 (3.2)	5.7 (6.0)	15.4 (15.1)	1880	430,300, 254
* 15.	1,10-Phen	Br	Cl	$[Ru(NO)Cl_2(AsPh_3)(OPhen)]^+Cl^-$ G 170	48.8 (49.7)	3.8 (3.9)	5.7 (5.8)	14.0 (14.6)	1880	430,300, 250
16.	$AsPh_3$	Br,I	Br	$[Ru(NO)Br_3(AsPh_3)_2].CH_2Cl_2$ O 240	40.7 (41.5)	3.1 (2.8)	1.8 (1.3)	30.4 (29.1)	1850	450,360, 300
17.	Py	Br,I	Br	$[Ru(NO)Br_3(AsPh_3)(Py)]$ Y 235	37.2 (36.5)	2.8 (2.6)	4.2 (3.7)	30.8 (31.7)	1850	450,350, 300

Table 2.1(contd.)

1	2	3	4	5	6	7	8	9	10	11
18.	4-Pic	Br,I	Br	$[Ru(NO)Br_3(AsPh_3)(Pic)]$ Y 230	37.4 (37.6)	3.4 (3.1)	3.1 (3.6)	31.4 (31.7)	1850	450,310, 260
*19.	2,2'-Bipy	Br,I	Br	$[Ru(NO)Br_2(AsPh_3)(Bipy)]^+Br^-$ G 195	39.5 (40.3)	2.5 (2.7)	4.5 (5.0)	28.2 (28.8)	1880	450,360, 310,230
*20.	1,10-Phen	Br,I	Br	$[Ru(NO)Br_2(AsPh_3)(OPhen)]^+Br^-$ G 190	42.6 (42.0)	3.2 (2.6)	5.6 (4.9)	29.2 (28.0)	1875	455,360, 310,250
21.	$AsPh_3$	Cl,Br,I	Br_3	$[Ru(NO)Br_3(AsPh_3)_2]$ O 240	44.4 (43.9)	3.4 (3.0)	1.8 (1.4)	25.2 (24.4)	1850	450,360, 300
22.	Py	Cl,Br,I	Br_3	$[Ru(NO)Br_3(AsPh_3)(Py)]$ Y 235	37.0 (36.5)	2.8 (2.6)	3.4 (3.7)	31.2 (31.7)	1850	450,350, 300
23.	4-Pic	Cl,Br,I	Br_3	$[Ru(NO)Br_3(AsPh_3)(Pic)]$ Y 230	38.4 (37.6)	4.0 (3.1)	3.8 (3.6)	30.4 (31.7)	1850	450,310, 260
*24.	2,2'-Bipy	Cl,Br,I	Br_3	$[Ru(NO)Br_2(AsPh_3)(Bipy)]^+Br^-$ G 195	40.6 (40.3)	3.0 (2.7)	4.8 (5.0)	28.0 (28.3)	1880	450,360, 310,230
*25.	1,10-Phen	Cl,Br,I	Br_3	$[Ru(NO)Br_2(AsPh_3)(OPhen)]^+Br^-$ G 190	41.8 (42.0)	2.0 (2.6)	5.2 (4.9)	27.5 (28.0)	1875	455,360, 310,250
26.	$AsPh_3$	CN	Cl	$[Ru(NO)CNCl_2(AsPh_3)_2]$ B 260	52.2 (52.8)	3.1 (3.7)	3.6 (3.3)	9.2 (8.4)	1860, 2040	432,335
27.	$AsPh_3$	CN,NCS	Cl	$[Ru(NO)Cl_3(AsPh_3)_2].\frac{1}{2}CH_2Cl_2$ OB >260	48.2 (49.1)	3.8 (3.5)	2.0 (1.5)	16.5 (15.9)	1860	430,353, 310,280

...contd.

Table 2.1(contd.)

1	2	3	4	5	6	7	8	9	10	11
28.	4-Pic	CN,NCS	Cl	$[Ru(NO)Cl_3(AsPh_3)(Pic)]$ YB 220	45.0 (45.2)	4.2 (3.6)	4.2 (4.3)	17.8 (16.6)	1860	435,390, 350,280, 200
29.	2,2'-Bipy	CN,NCS	Cl	$[Ru(NO)Cl_2(AsPh_3)(Bipy)]^+Cl^-$ G 180	48.8 (48.0)	3.8 (3.2)	6.8 (6.0)	16.2 (15.1)	1880	430,390, 285
30.	1,10-Phen	CN,NCS	Cl	$[Ru(NO)Cl_2(AsPh_3)(OPhen)]^+Cl^-$ G 170	49.2 (49.7)	3.8 (3.1)	5.4 (5.8)	14.2 (14.6)	1880	445,345, 300,275
31.	$AsPh_3$	CN,NCS	Br,Br_3	$[Ru(NO)Br_3(AsPh_3)_2].CH_2Cl_2$ O 240	42.0 (41.5)	3.2 (3.0)	1.6 (1.3)	30.5 (29.1)	1850	450,360, 300,230
32.	Py	CN,NCS	Br,Br_3	$[Ru(NO)Br_3(AsPh_3)(Py)]$ Y 235	36.2 (36.5)	3.2 (3.6)	4.8 (3.7)	29.5 (31.7)	1850	450,350, 300,230
33.	2,2'-Bipy	CN,NCS	Br,Br_3	$[Ru(NO)Br_2(AsPh_3)(Bipy)]^+Br^-$ G 196	37.2 (37.8)	3.4 (2.7)	5.2 (4.5)	33.1 (33.8)	1880	450,360, 310,230
34.	1,10-OPhen	CN,NCS	Br,Br_3	$[Ru(NO)Br_2(AsPh_3)(OPhen)]^+Br^-$ G 190	41.8 (42.0)	2.0 (2.6)	5.2 (4.9)	28.4 (28.0)	1875	455,360, 310,250
35.	PPh_3	Cl,I	Cl	$[Ru(NO)Cl_3(AsPh_3)(PPh_3)]$ O 215	54.1 (53.6)	3.4 (3.7)	1.9 (1.7)	12.5 (13.1)	1850	430,370, 350,290
36.	PPh_3	Br	Cl	$[Ru(NO)BrCl_2(AsPh_3)(PPh_3)$ O 218	50.2 (50.7)	3.6 (3.5)	1.8 (1.6)	18.2 (17.7)	1850	430,350, 300,280
37.	PPh_3	CN	Cl	$[Ru(NO)CNCl_2(AsPh_3)(PPh_3)]$ B 230	55.2 (55.9)	3.4 (3.7)	3.8 (3.5)	9.6 (8.9)	1860, 2040	430,335

...contd.

Table 2.1 (contd.)

1	2	3	4	5	6	7	8	9	10	11
38.	PPh_3	NCS	Cl	$[Ru(NO)Cl_3(AsPh_3)(PPh_3)]$ O 215	53.2 (53.6)	3.2 (3.7)	2.0 (1.7)	13.5 (13.1)	1850	430,370,350, 290
39.	PPh_3	Cl	Br	$[Ru(NO)ClBr_2(AsPh_3)(PPh_3)]$ O 217	48.8 (48.2)	3.8 (3.3)	2.0 (1.6)	22.4 (21.9)	1850	430,340,310, 270
40.	PPh_3	Br,I,CN,NCS	Br,Br_3	$[Ru(NO)Br_3(AsPh_3)(PPh_3)]$ O 210	46.4 (46.0)	3.8 (3.1)	2.2 (1.4)	26.4 (25.5)	1850	460,350,300
	E = Sb									
41.	$SbPh_3$	Cl,I	Cl	$[Ru(NO)Cl_3(SbPh_3)_2]$ Y 220(d)	46.2 (45.7)	3.8 (3.1)	1.8 (1.4)	12.2 (11.1)	1840	435,360,315, 270
42.	Py	Cl,I	Cl	$[Ru(NO)Cl_3(SbPh_3)(Py)]$ Y 202	40.6 (41.2)	3.8 (3.0)	4.8 (4.1)	16.2 (15.8)	1840	455,320,280
43.	4-Pic	Cl,I	Cl	$[Ru(NO)Cl_3(SbPh_3)(Pic)]$ Y 200	41.6 (42.1)	3.8 (3.3)	4.6 (4.0)	16.0 (15.4)	1840	455,320,285
44.	2,2'-Bipy	Cl,I	Cl	$[Ru(NO)Cl_2(SbPh_3)Bipy]^+Cl^-$ GB 180	46.2 (45.0)	3.8 (3.0)	6.0 (5.6)	15.4 (14.2)	1880	435,360,310, 280
45.	1,10-Phen	Cl,I	Cl	$[Ru(NO)Cl_2(SbPh_3)(OPhen)]^+Cl^-$ GB 175	47.4 (46.6)	3.9 (3.0)	5.8 (5.4)	13.9 (13.7)	1880	435,360,310, 280
46.	$SbPh_3$	Br	Cl	$[Ru(NO)BrCl_2(SbPh_3)_2]$ O 200	42.8 (43.7)	3.4 (3.0)	1.6 (1.4)	16.1 (15.4)	1850	435,360,315, 270
47.	Py	Br	Cl	$[Ru(NO)BrCl_2(SbPh_3)(Py)]$ Y 202	38.1 (38.6)	3.8 (3.2)	4.4 (3.9)	22.0 (21.1)	1850	435,355,280

...contd.

Table 2.1 (contd.)

1	2	3	4	5	6	7	8	9	10	11
48.	Pic	Br	Cl	$[Ru(NO)BrCl_2(SbPh_3)(Pic)]$ YB 204	38.8 (39.5)	3.6 (3.5)	4.2 (3.8)	21.2 (20.7)	1850	
* 49.	2,2'-Bipy	Br	Cl	$[Ru(NO)Cl_2(SbPh_3)Bipy]^+Cl^-$ YB 180	45.6 (45.0)	3.4 (3.0)	5.8 (5.6)	14.4 (14.2)	1880	435,350,310, 260
* 50.	1,10-Phen	Br	Cl	$[Ru(NO)Cl_2(SbPh_3)(OPhen)]^+Cl^-$ B 175	46.2 (46.8)	3.2 (3.0)	5.6 (5.4)	14.2 (13.7)	1880	440,350,300, 260
51.	$SbPh_3$	Cl	Br	$[Ru(NO)ClBr_2(SbPh_3)_2]$ Y 220(d)	42.6 (41.9)	3.4 (2.9)	1.8 (1.3)	18.2 (19.0)	1850	440,350,280
52.	Py	Cl	Br	$[Ru(NO)ClBr_2(SbPh_3)(Py)]$ Y 200	37.1 (36.3)	3.8 (3.0)	3.2 (3.6)	24.8 (25.7)	1850	440,350,285
53.	$SbPh_3$	Cl,I	Br_3	$[Ru(NO)Br_3(SbPh_3)_2]$ O 230	41.0 (40.1)	3.2 (2.7)	1.8 (1.3)	21.5 (22.2)	1860	390,340,300, 255
* 54.	2,2'-Bipy	Cl,Br	Br,Br_3	$[Ru(NO)Br_2(SbPh_3)Bipy]^+Br^-$ G 180	38.4 (38.1)	2.8 (2.6)	4.2 (4.7)	26.5 (27.2)	1880	400,360,300, 280
* 55.	1,10-Phen	Cl,Br	Br,Br_3	$[Ru(NO)Br_2(SbPh_3)(OPhen)]^+Br^-$ G 170	40.4 (39.8)	2.8 (2.5)	4.2 (4.6)	27.2 (26.5)	1880	400,360,310, 280
56.	$SbPh_3$	CN	Cl	$[Ru(NO)CNCl_2(SbPh_3)_2]$ B >270	48.4 (47.5)	3.6 (3.2)	3.2 (2.9)	8.6 (7.5)	1860, 2040	440,335,320

...contd.

Table 2.1 (contd.)

1	2	3	4	5	6	7	8	9	10	11
57.	$SbPh_3$	CN	Br, Br_3	$[Ru(NO)CNBr_2(SbPh_3)_2]$ B >270	44.2 (43.4)	3.4 (2.9)	3.2 (2.7)	16.5 (15.6)	1860	440, 330, 310
58.	$SbPh_3$	NCS	Cl	$[Ru(NO)(NCS)Cl_2(SbPh_3)_2]$ B 142	46.4 (45.9)	3.4 (3.1)	2.6 (2.8)	8.2 (7.3)	1870, 2100	

O=Orange, G=Green, YB=Yellowish Brown, Y=Yellow, B=Brown,

M.P. are uncorrected.

2,2'-Bipy = 2,2'-Bipyridine, 1,10-Phen = 1,10 = Phenanthroline, Py = Pyridine, γ-Pic = γ-Picoline

* Cationic complexes $[Ru(\eta^5-C_5H_5)(EPh_3)(L-L]^+X^-$ (L-L = 2,2'-Bipy, 1,10-Phen).

CAPTIONS FOR THE FIGURES

Infrared spectra of the complexes

Fig. 2.1 (1) $[Ru(NO)Cl_3(AsPh_3)_2]$

(2) $[Ru(NO)Br_3(AsPh_3)(py)]$

(3) $[Ru(NO)Cl_2(AsPh_3)(OPhen)]^+Cl^-$

(4) $[Ru(NO)Cl_3(SbPh_3)_2]$

Fig. 2.2 (5) $[Ru(NO)Br_3(SbPh_3)_2]$

(6) $[Ru(NO)Br_2(SbPh_3)(Bipy)]^+Br^-$

Fig. 2.3 (7) $[Ru(NO)CNCl_2(AsPh_3)_2]$

(8) $[Ru(NO)(NCS)Cl_2(SbPh_3)_2]$

Electronic spectra of the complexes

Fig. 2.4 (a) $[Ru(NO)Cl_3(AsPh_3)_2]$

(b) $[Ru(NO)Cl_3(SbPh_3)_2]$

Fig. 2.5 (c) $[Ru(NO)Br_3(AsPh_3)_2]$

(d) $[Ru(NO)Br_3(SbPh_3)_2]$

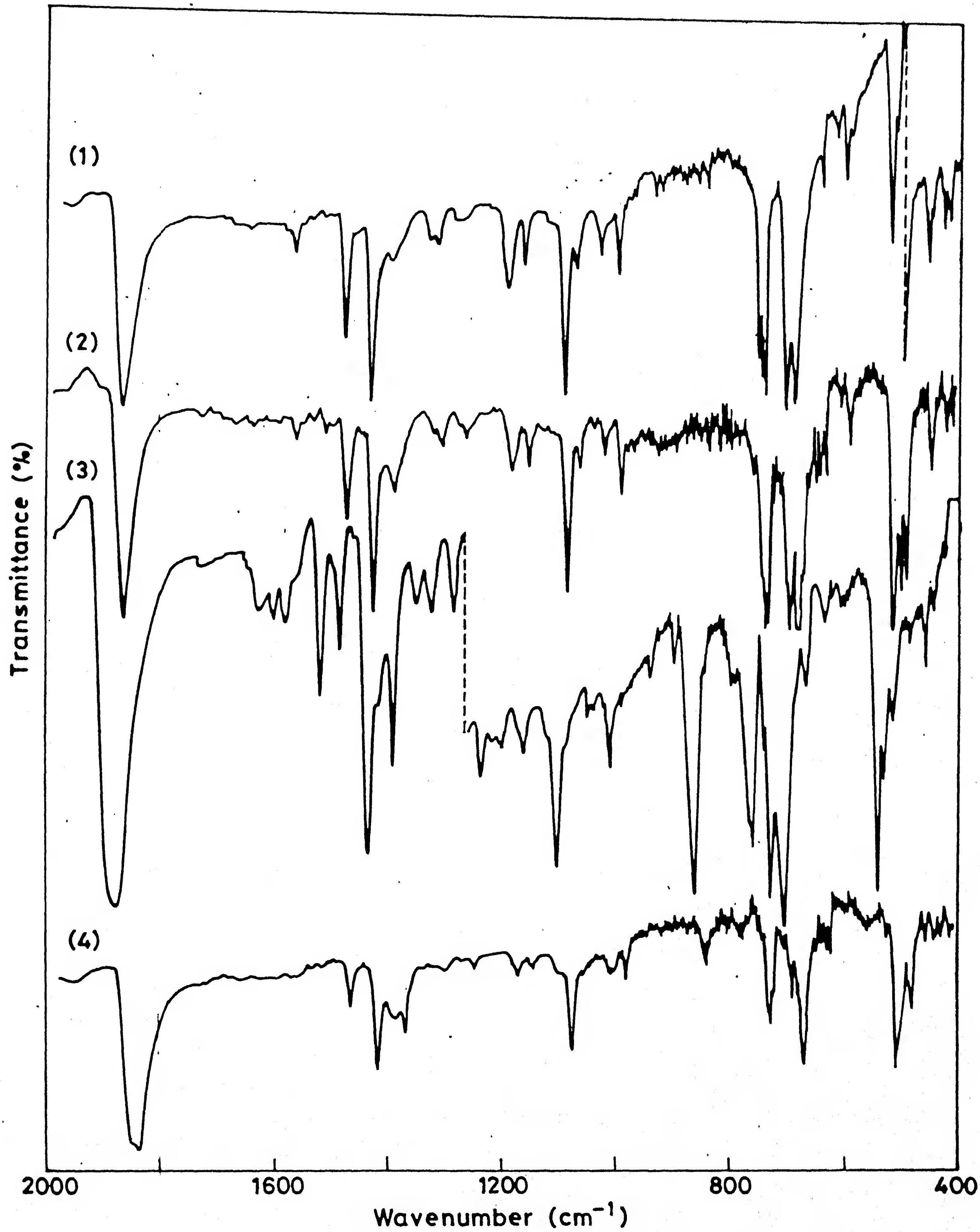

Fig. 2.1 Infrared spectra.

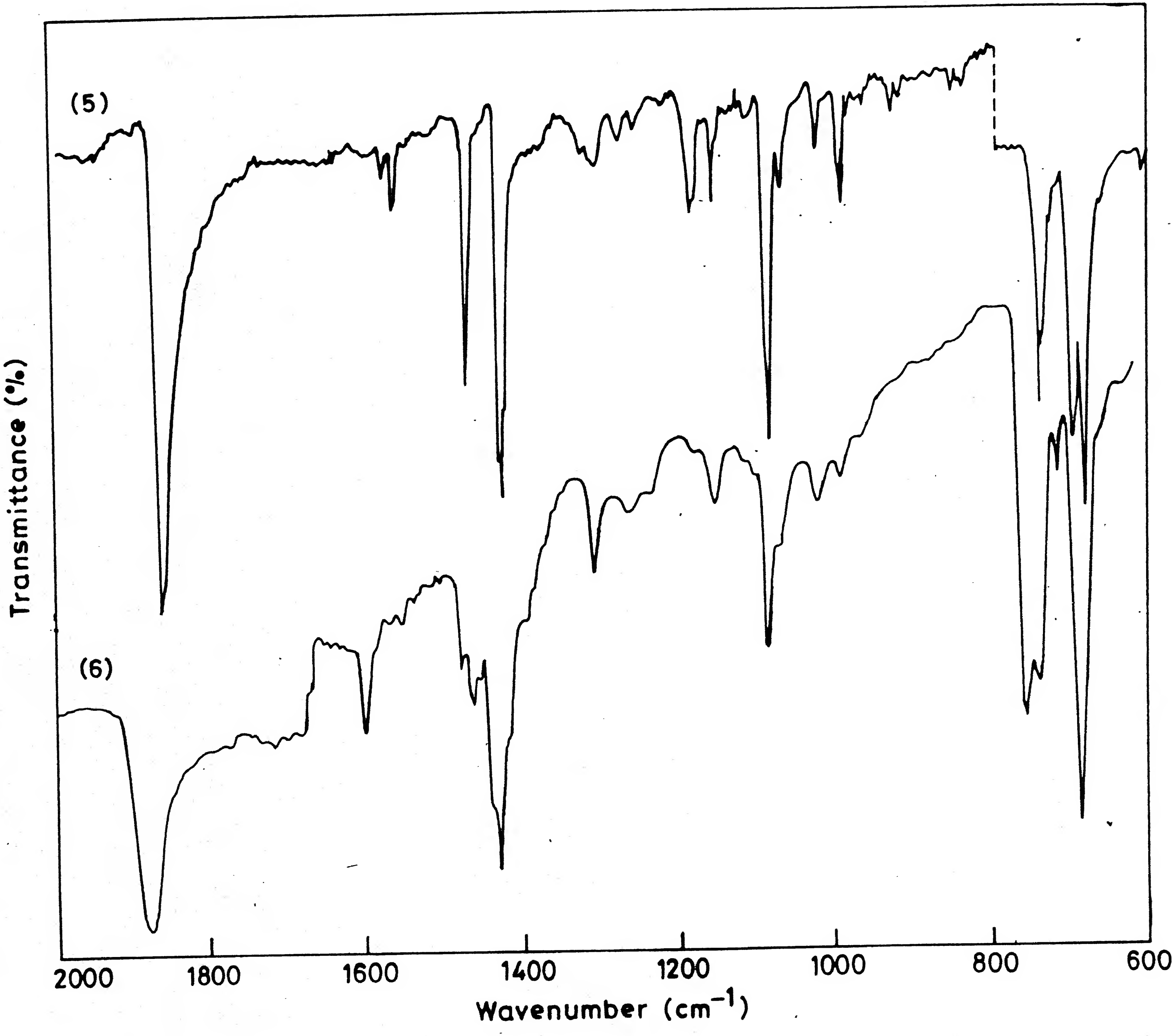

Fig. 2.2 Infrared spectra.

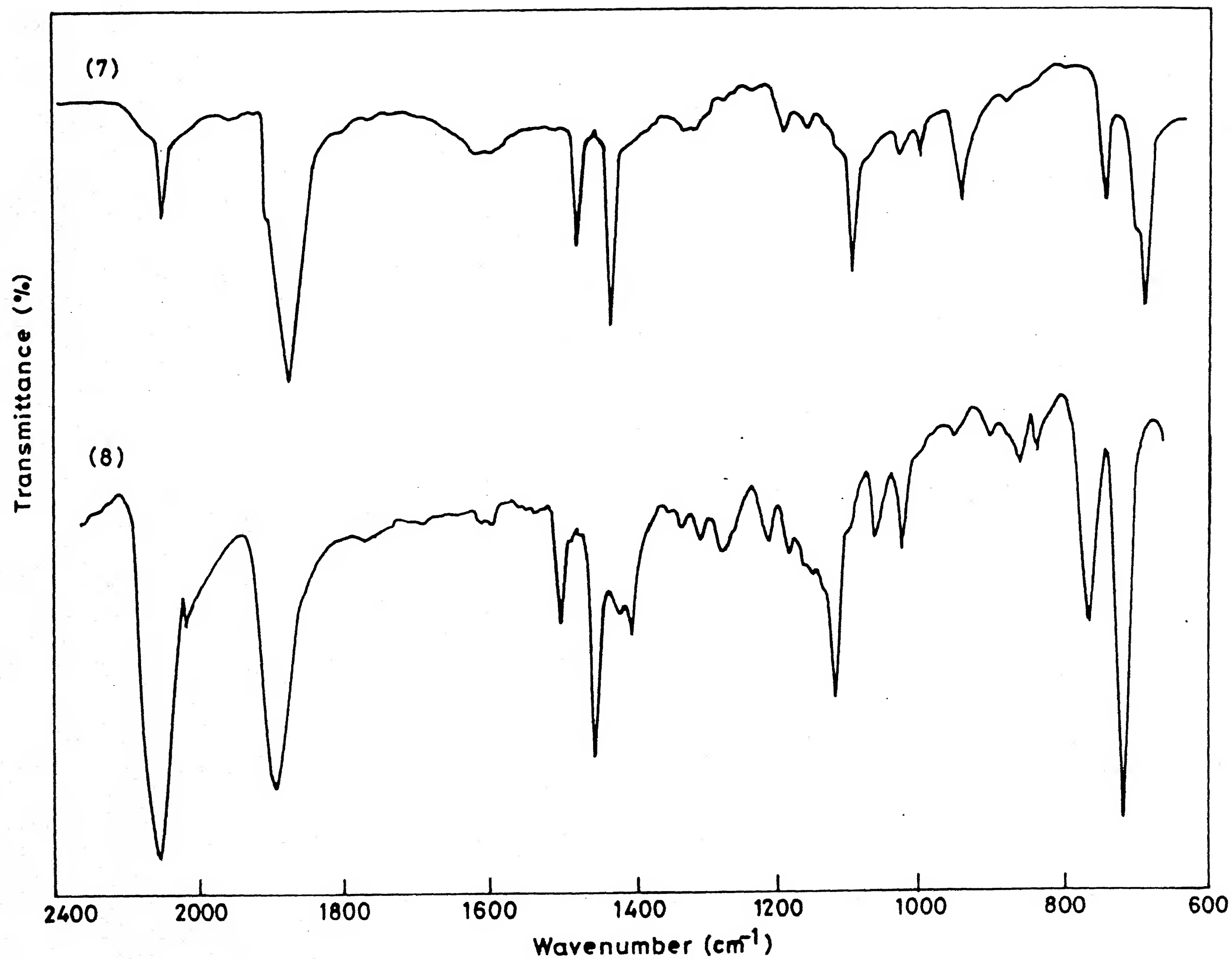

Fig. 2.3 Infrared spectra.

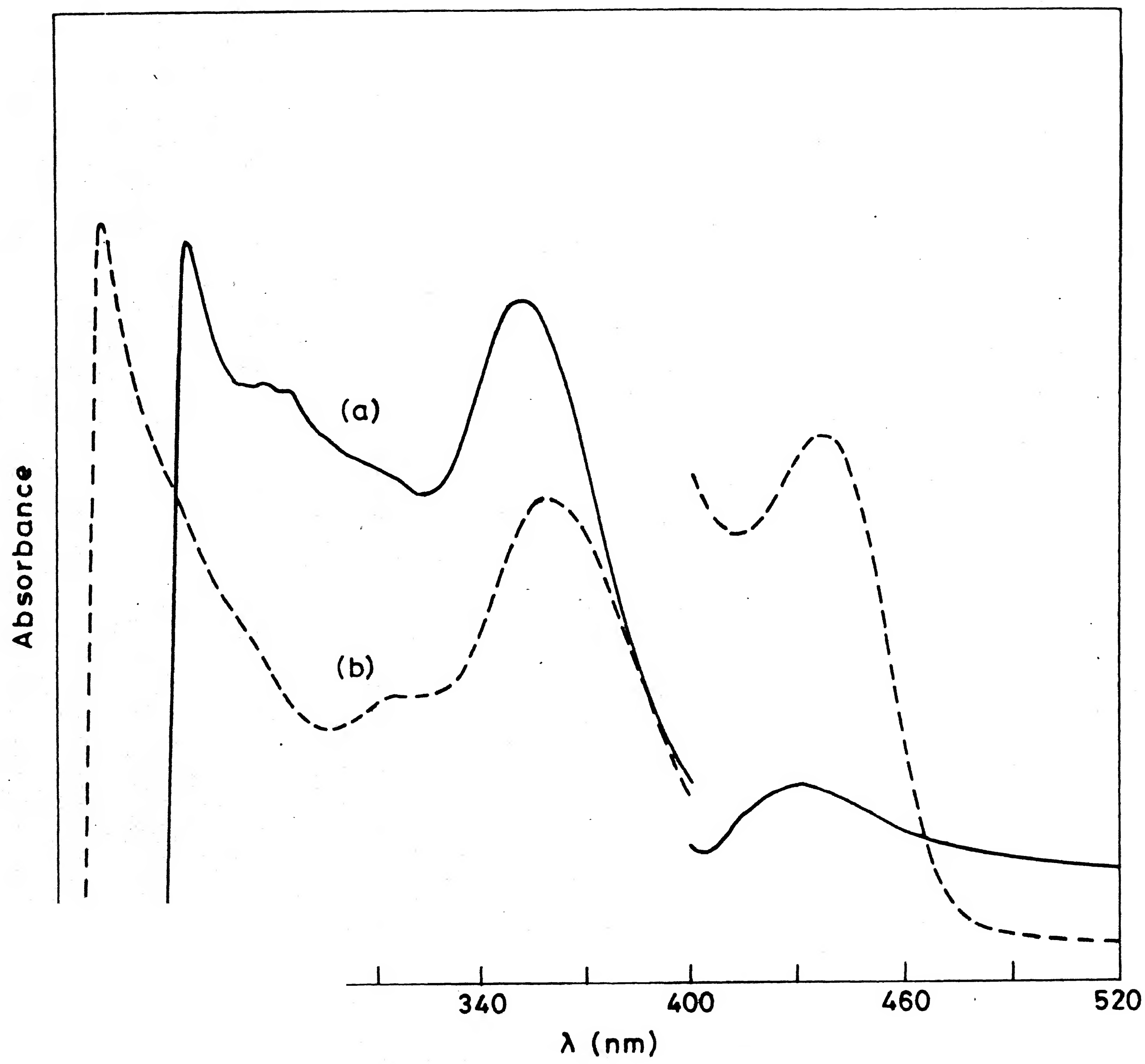

Fig. 2.4 Electronic specta.

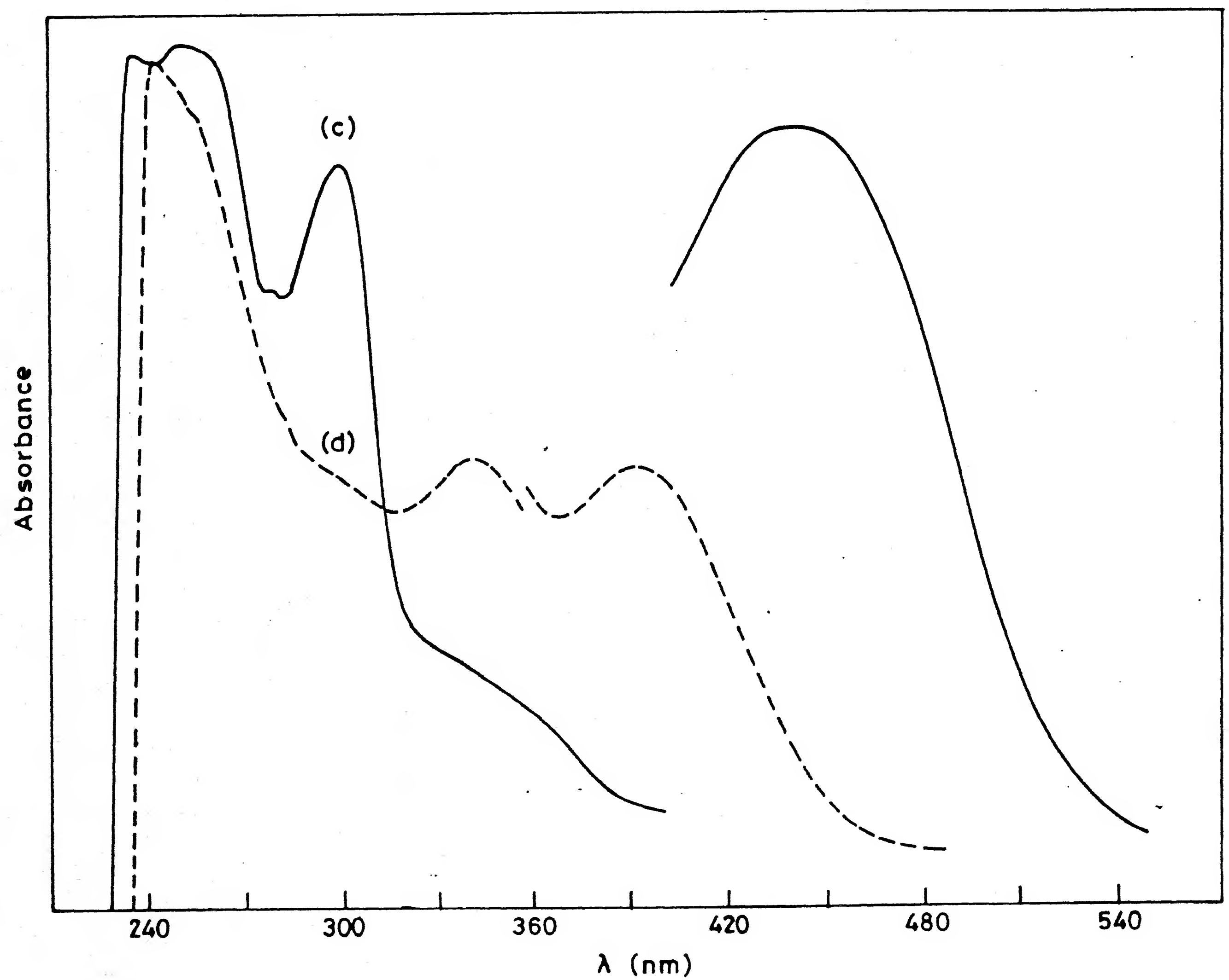

Fig. 2.5 Electronic spectra.

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Chapter - III

Reactions of NOX ($X = Cl^-$, Br^-, Br_3^-) with Cyclopentadienyl Ruthenium Complexes having trichlorostannate as Coligand

3.1 Introduction

Previous study[1] of nitrosylation reactions of $[Ru(\eta^5-C_5H_5)X(PPh_3)_2]$ ($X = Cl^-$, Br^-, I^-, CN^-, SCN^-) by NOX ($X = Cl^-$, Br^-, Br_3^-) revealed the formation of $[Ru(NO)X_nBr_{3-n}(PPh_3)_2]$ ($X = Cl$, Br; $n = 0-3$). The same reaction with $[Ru(\eta^5-C_5H_5)SnCl_3-(PPh_3)_2]$ yielded $[Ru(NO_2)SnCl_3)(PPh_3)\{(\pi-C_6H_5)PPh_2\}]$. Although the role played by the strong π-acids, like $SnCl_3^-$ and/or NO_2^- in changing the course of the reaction is still obscure, but apparently the reaction path is dependent upon a delicate balance of various electronic or/and steric factors of the reactants. This prompted us to extend further the study of these reactions. Besides, the basic character of the phosphorous atom of the π-bonded phosphorous $[\pi-C_6H_5)PPh_2]$ towards other metal center is also lost to an extent that it remains uncoordinated with other metal ions.

It has now been well established that there exists a gradual variation in σ-basic and π-acid characters of P, As, Sb in EPh_3 and other heterocyclic molecules.[2] On account of this variation it may be possible to find factors responsible for the changes that take place in the reaction path. Thus, if a systematic study of these reactions could be carried out with analogous molecules having co-ligands like $AsPh_3$, $SbPh_3$ and/or other heterocyclic bases, results of these reactions may contribute a little to the answer of question as: why does Ru(II) bonded with strong π-acids like $SnCl_3^-$ or/and NO_2^- exhibit an unusual and different behaviour, not accessible by those when it is bonded with anions like Cl^-, Br^- or I^- (π-bases) or CN^-, SCN^- (weaker π-acids)?

This chapter concerns with the results of the reactions of $[Ru(\eta^5\text{-}C_5H_5)SnCl_3(EPh_3)L]$ or $[Ru(\eta^5\text{-}C_5H_5)(EPh_3)L\text{-}L]SnCl_3$ (E = As, Sb; L = $AsPh_3$, $SbPh_3$, PPh_3, pyridine, γ-picoline; L-L=2,2'-bipyridine 1,10-phenanthroline) with NOX (X = Cl^-, Br^-, Br_3^-) and characterizations of the reaction products.

3.2 Experimental

All the reagents were of Analar grade. The solvents were distilled and dried before use. NOX (X = Cl^-, Br^-, Br_3^-), $[Ru(\eta^5\text{-}C_5H_5)SnCl_3(EPh_3)_2]$ (E = P, As, Sb), $[Ru(\eta^5\text{-}C_5H_5)SnCl_3\text{-}(EPh_3)L]$ (L = py, γ-pic), $[Ru(\eta^5\text{-}C_5H_5)(PPh_3)L\text{-}L]^+SnCl_3^-$ (L-L = 2,2'-bipy, 1,10-phen) were prepared as reported in the literature.[3-8]

(A) Preparation of Complexes

1. Reactions of NOX ($X = Cl^-$, Br^-, Br_3^-) with $[Ru(\eta^5-C_5H_5)SnCl_3-(EPh_3)(E'Ph_3)]$ ($E = As$; $E' = As, P$)

(i) Bright yellow coloured crystals of $[Ru(\eta^5-C_5H_5)SnCl_3(EPh_3)-(E'Ph_3)]$ (ca. 0.2 mmol) dissolved in 40 ml of methanol and dichloromethane (2:1 , v/v) mixture were refluxed with 5 ml of saturated dichloromethane solution of NOX for 2 hours where upon orange-red shining microcrystals (I) were separated. They were filtered, washed with methanol, ether, dried under vacuum and analysed.

(ii) The orange-red microcrystals (I) were dissolved in 25 ml of $CHCl_3$, followed by the addition of about 100 mg of EPh_3 ($E=P$, As) in it. The reaction mixture was heated to reflux for 2 hours. The resulting solution was concentrated to about 10 ml and excess of methanol was added to it. This led to the precipitation of $[Ru(NO)X_3(EPh_3)_2]$ ($X = Cl^-$, Br^-). It was filtered and the filtrate was kept for a few hours, whereupon orange red microcrystals of $[Ru(NO_2)SnCl_3(EPh_3)-\{(\pi-C_6H_5)EPh_2\}]$ were separated out. These were repeatedly re-crystallized to finally yield pure orange-red crystals.

2. Reactions of NOX ($X = Cl^-$, Br^-) with $[Ru(\eta^5-C_5H_5)SnCl_3(SbPh_3)_2]$

(i) A solution (40 ml) of the complex $[Ru(\eta^5-C_5H_5)SnCl_3(SbPh_3)_2]$

(0.12 mmol) in methanol:dichloromethane mixture (2:1, v/v) was mixed with a saturated dichloromethane solution of NOX (5 ml). The resulting mixture was refluxed for two hours. The reddish-pink solution, thus obtained, was concentrated to about 5 ml on a water bath. Addition of 20 ml of hexane resulted in the precipitation of a pink coloured compound $[Ru(NO)(NO_2)_2X(SbPh_3)]$ ($X = Cl^-, Br^-$) which was repeatedly recrystallised with dichloromethane/hexane (yield, ~30%).

(ii) 0.2 mmol of $[Ru(\eta^5-C_5H_5)SnCl_3(SbPh_3)_2]$ was dissolved in a mixture of 20 ml of dichloromethane and 30 ml of methanol. A saturated solution of NOX in CH_2Cl_2 (10 ml) and 0.1 g of $SbPh_3$ was added to the solution. The reaction mixture was refluxed for about two hours. The resulting solution was concentrated, whereupon orange-shining microcrystals of $[Ru(NO)X_3(SbPh_3)_2]$ ($X = Cl^-, Br^-$) were separated out. These were separated by centrifugation, washed with methanol, ether and dried under vacuum. (yield, ~80%).

From the filtrate, the orange red crystals of $[Ru(NO_2)SnCl_3(SbPh_3)\{(\pi-C_6H_5)SbPh_2\}]$ were obtained slowly in a very low yield (*ca.* 5-10%).

(3) <u>Reactions of NOX ($X = Cl^-, Br^-, Br_3^-$) with $[Ru(\eta^5-C_5H_5)SnCl_3(AsPh_3)L]$ (L = py, γ-pic) and $[Ru(\eta^5-C_5H_5)(AsPh_3)L-L]^+SnCl_3^-$ (L-L = 2,2'-bipy, 1,10-phen)</u>

A saturated solution of NOX in CH_2Cl_2 (10 ml) was added

slowly to a solution of appropriate complex (ca. 0.2 mmol) in a mixed solvent of methanol:dichloromethane (2:1, v/v). The resulting solution was heated under reflux for two hours, whereupon microcrystals of the corresponding complex (I) in very low yield (~25%) were obtained. The product was filtered, washed with methanol, ether and dried under vacuum. From these crystals the π-bonded compound $[Ru(NO_2)SnCl_3(AsPh_3)\{(\pi-C_6H_5)AsPh_2\}]$ was separated by the procedure mentioned in (1).

The filtrate was concentrated to about 5 ml. Addition of n-hexane to the concentrated solution yielded $[Ru(NO)X_3(AsPh_3)L]$ (L = Py, γ-Pic)/$[Ru(NO)(NO_2)X_2L\text{-}L]$ (L-L' = 2,2'-bipy, 1,10-phen) (yield, ca. 40%).

(4) Reactions of NOX (Cl^-, Br^-) with $[Ru(\eta^5-C_5H_5)(SbPh_3)L\text{-}L]^+SnCl_3^-$ (L-L = 2,2'-bipy, 1,10-phen)

0.1 mmol of $[Ru(\eta^5-C_5H_5)(SbPh_3)L\text{-}L]^+SnCl_3^-$ was dissolved in a mixture containing 10 ml dichloromethane and 25 ml of methanol. A saturated solution of NOX in CH_2Cl_2 (5 ml) was added to the solution and the reaction mixture was heated under reflux for about 3 hours. A brown compound $[Ru(NO)X_3(L\text{-}L)]$ which crystallised out of solution, was filtered, washed with methanol, ether and dried under vacuum (yield, ca. 40%).

(5) Reactions of NOX ($X = Cl^-$, Br^-) with $[Ru(\eta^5-C_5H_5)SnCl_3(SbPh_3)L]$ (L = py, γ-pic)

A saturated solution of NOX in dichloromethane (5 ml), to a solution of $[Ru(\eta^5-C_5H_5)SnCl_3(SbPh_3)L]$ (0.12 mmol) in a mixed solvent containing $MeOH:CH_2Cl_2$ (2:1, v/v) was added slowly and the reaction mixture was allowed to reflux for two hours. Yellowish brown microcrystals of $[Ru(NO)X_3(SbPh_3)L]$ in low yield were separated out. They were filtered, washed with methanol, ether and dried under vacuum (yield, ca. 20%).

The reactions of $[Ru(\eta^5-C_5H_5)SnCl_3(SbPh_3)_2]$ and its derivatives with $NOBr_3$ did not yield pure products even after repeated recrystallisation.

(6) Reactions of $[Ru(NO_2)SnCl_3(EPh_3)\{(\pi-C_6H_5)EPh_2\}]$ (E = P, As) with pyridine

$[Ru(NO_2)SnCl_3(EPh_3)\{(\pi-C_6H_5)EPh_2\}]$ (ca. 0.1 mmol) was dissolved in 25 ml of $CHCl_3$ in which 4 ml of pyridine was added. The reaction mixture was refluxed for 3 hours. Yellow brown microcrystals of $[RuCl_2(Py)_4]$ were separated out. These were filtered, washed with methanol, ether and dried. The remaining solution was concentrated to near dryness, triphenylarsine or triphenylphosphine was obtained after the addition of n-hexane to the semidried mass.

(B) Analyses and Measurements

Carbon, hydrogen, nitrogen, halogens and sulphur analyses, melting points, magnetic measurements, infrared, ^{1}H nmr and electronic spectra were carried out according to the methods given in chapter II.

3.3 Results and Discussion

The behaviour of the complexes $[Ru(\eta^5-C_5H_5)SnCl_3(EPh_3)_2]$ (E = P, As, Sb) was somewhat different from one other in their reactivity towards NOX. Although it has been reported earlier[1] that treatment of $[Ru(\eta^5-C_5H_5)SnCl_3(PPh_3)_2]$ with NOX leads to the formation of solely π-bonded complex $[Ru(NO_2)SnCl_3(PPh_3)\{(\pi-C_6H_5)-PPh_2\}]$ in good yield, but the addition of a little PPh_3 to the reaction mixture yielded $[Ru(NO)X_3(PPh_3)_2]$ also in small yield along with a large yield of π-bonded PPh_3 complex. Interaction of $[Ru(\eta^5-C_5H_5)SnCl_3(EPh_3)(E'Ph_3)]$ (E = As; E' = As, P) with NOX led to the formation of red products (I) which exhibited in their IR spectra bands due to (ν_{NO}), (ν_{NO_2}), π-bonded phenyl group and phenyl groups. We believe these compounds (I) to be either a mixture of $[Ru(NO_2)SnCl_3(EPh_3)\{(\pi-C_6H_5)EPh_2\}]$ and $[Ru(NO)Cl_3(EPh_3)_2]$ (E = As or P) (40% and 60%) or an addition compound as suggested by their analyses. Addition of EPh_3 (E = P, As) to the reaction mixture led to the formation of $[Ru(NO_2)SnCl_3(EPh_3)\{(\pi-C_6H_5)EPh_2\}]$ and $[Ru(NO)X_3(EPh_3)_2]$. All attempts to separate them from the

red complex by column chromatography failed. The only method of separating them and getting pure products was to carry out the reactions of I in the presence of a little amount of EPh_3.

Reactions of $[Ru(\eta^5-C_5H_5)SnCl_3(SbPh_3)_2]$ with NOX did not yield any product having π-bonded phenyl group bonded to the ruthenium. They led to the formation of a pink compound analysed for $[Ru(NO)(NO_2)_2Cl(SbPh_3)]$. Addition of $SbPh_3$ to the reaction mixture (Exptl. Section) however afforded two compounds $[Ru(NO)X_3-(SbPh_3)_2]$ and $(Ru(NO_2)SnCl_3(SbPh_3)\{(\pi-C_6H_5)SbPh_2\}]$ with their yields in the ratio of 8:1. In other reactions of the complexes containing $SbPh_3$, π-bonded $SbPh_3$ product was also not obtained.

The results suggest that under the reaction conditions atleast two parallel reactions leading to the (1) formation of nitrosyl and (2) that of π-bonded complex are going on. However, the rates of their formations are dependent on the coligands. The difference in the behaviour of these complexes towards the π-complex formation parallels that of the σ-basicity of the phosphine, arsine and stibine ($PPh_3 > AsPh_3 > SbPh_3$). It is further suggested that interaction of NOX possibly led to oxidation of EPh_3 group also, followed by the decomposition of the complexes besides nitrosylation reaction. Presumably nitrosylation reaction is, in general, faster than that of the oxidation of EPh_3. Since the rate of oxidation of EPh_3 (E = P, As, Sb) is in the order $PPh_3 < AsPh_3 < SbPh_3$, the rate of triphenylphosphine oxidation is relatively

slower compared to those of $AsPh_3$ and $SbPh_3$ which in turn, result in the concentration of the coordinated base EPh_3 in the reaction mixture in the order as $PPh_3 > AsPh_3 > SbPh_3$ yielding the π-bonded arene reaction products in the same order.

The difference in the reactivity of EPh_3 parallels the order of their π-acidity ($PPh_3 > AsPh_3 > SbPh_3$). The NO_2^-, $SnCl_3^-$, EPh_3 have electron withdrawing power comparable to $Cr(CO)_3$ moiety in $ArCr(CO)_3$.[9,10,11] Furthermore, the effect on the metal to ligand e.g. interaction by replacing a π-C_5H_5 with a π-C_6H_6 ligand has also been shown to be greater which may play an important role in the formation of π-complexes.[12] This may further explain the decreasing order of the π-bonded complex in these reactions ($PPh_3 >$ $AsPh_3 > SbPh_3$).

The reactions of $[Ru(\eta^5\text{-}C_5H_5)EPh_3(L\text{-}L)]^+SnCl_3^-$ and $[Ru(\eta^5\text{-}C_5H_5)SnCl_3(EPh_3)L]$ (E = P, As) with NOX led to the formation of $[Ru(NO_2)SnCl_3(EPh_3)\{(\pi\text{-}C_6H_5)EPh_2\}]$ in low yield (~20%). From the filtrate the isolated products were $[Ru(NO)(NO_2)X_2(L\text{-}L)]$ and $[Ru(NO)X_3(EPh_3)L]$. The reactions with $SbPh_3$ complexes did not give any π-bonded product. The products obtained were only nitrosyl complexes, $[Ru(NO)X_3(L\text{-}L)]$ and $[Ru(NO)X_3(SbPh_3)L]$. In our previous report[1] we described that the reactions of $[Ru(\eta^5\text{-}C_5H_5)(SnCl_3)(PPh_3)(L\text{-}L)_{1/2}]$ lead to the formation of $[Ru(NO_2)SnCl_3\{(\pi\text{-}C_6H_5)PPh_2\}(L\text{-}L)_{1/2}]$. Further attempts to react cyclopentadienyl ruthenium complexes with triphenylarsine and triphenylstibine as

reported elsewhere[8] showed that EPh_3 (E = P, As, Sb) on prolonged refluxing afforded complexes $[Ru(\eta^5-C_5H_5)(PPh_3)(L-L)]^+SnCl_3^-$. Reactions of $[Ru(\eta^5-C_5H_5)(PPh_3)(L-L)]SnCl_3$ with NOX behaved similar to their arsine analogues. The reason for this behaviour may be that the reactions of the complexes with NOX effecting the removal of cyclopentadienyl anion and EPh_3 molecule created four vacant coordination sites in the case of 2,2'-bipy, 1,10-phen. These vacant sites were subsequently occupied by NO, NO_2 and X ($X = Cl^-$, Br^-). In the reactions of pyridine and 4-picoline complexes the cyclopentadiene moiety was substituted by NO and X. At the same time, a parallel reaction with the formation of π-bonded complexes also ensues. The formation of π-bonded complexes was faster in the case of PPh_3 compared to those of $AsPh_3$ complexes. $SbPh_3$ complexes does not form any π-bonded complexes in the reaction of complexes having heterocyclic bases as one of the ligands with NOX. It, thus, gave further evidence to the reason of the different behaviour of PPh_3, $AsPh_3$, $SbPh_3$ towards the formation of π-bonded complexes. The analytical data of the complexes were given in Table 3.1.

All the reaction products have been characterized by the spectroscopic methods briefly described in the following paragraphs.

IR Spectra

The spectra of all the complexes exhibited bands arising from the vibrational modes of the spectator ligands, viz. EPh_3

(E = P, As, Sb) molecule, NO^+, NO_2^- etc. The spectra of [Ru(NO_2)-$SnCl_3$(EPh_3)$\{(\pi-C_6H_5)EPh_2\}$] have other features not occurring in the spectra of nitrosyl complexes.

The complexes [Ru(NO)X_3(EPh_3)L] and [Ru(NO)X_3L-L] shows intense absorption band in the region 1870–1840 cm^{-1} which is characteristic of a terminal nitrosyl group. It did not appear in the spectra of the π-bonded complexes. Instead four new bands around (1340, 1320, 850, 300(W) cm^{-1}) consistently appeared in all the spectra. The positions of these bands suggested the presence of NO_2^- group bonded to ruthenium.[13] Since NO_2^- may coordinate both as nitro or nitrito group, the absence of the diagonistic band due to wagging mode of vibration of nitro groups around 650 cm^{-1} unless masked by the intense EPh_3 bands around 600 cm^{-1} was tentatively taken as evidence for its being bonded to the metal ion through oxygen.

Another interesting aspect in their ir spectra has been the presence of five strong bands in the 1510–1350 cm^{-1}, and three bands in the 820–690 cm^{-1} regions. These bands indicated that one of the phenyl rings of EPh_3 is coordinated to the metal ion through π-bonded interaction.[14–20] Therefore, the bonding in the complexes were regarded as η^6-interaction using all the 6 electrons of the phenyl ring in bonding to the metal. Since one of the phenyl groups of EPh_3 is donating electron density to metal through π-bonding, one should also expect a change in the position of the out of plane C-H bending mode. Such a shift in the band position

has been observed in 820–690 cm^{-1} region, not present in the spectra of those where EPh_3 is bonded to metal through σ bond. It has therefore, been assumed that the new extra band around 800 cm^{-1} arises due to (γ_{C-H}) of phenyl ring π–bonded to the metal center. The bands in the region 550–480 cm^{-1} are also very much complicated for π–bonded complexes compared to those which do not contain π–bonded phenyl rings. It consisted of a group of six adjacent sharp bands which is the characteristic of a π–bonded system.[19]

The characteristic bands of triphenyl–arsine and triphenyl–stibine (1480, 1430, 1100s, 700s, 530s cm^{-1}) together with those of heterocyclic bases, viz. pyridine (1590, 1583, 1441, 1148, 1085, 735 cm^{-1}), γ–picoline (1600, 1505, 820, 720–730 cm^{-1}), 2,2'–bi–pyridine (1590, 1435, 1420, 730–740 cm^{-1}) and 1,10–phenanthroline (1600,1430,840s,740–720 cm^{-1}) were observed in the spectra of nitrosyl complexes.

NMR Spectra

The nmr spectra of the complexes $[Ru(NO_2)SnCl_3(EPh_3)\{(\pi-C_6H_5)EPh_2\}]$ showed the following bands due to different protons in the complexes. The normal resonances arising from the phenyl group of the EPh_3 (E = P, As, Sb) ligands were present in the region (δ 7–8.5 ppm). A broadened doublet at (δ 5.1 ppm) and a triplet at (δ 4.3 ppm) were due to H^3 and H^2 protons of π–arene phenyl group (Fig.3.1). The H^1 absorption is hidden under the

other phenyl group absorptions. It is well established[13,19] that the presence of π-bonding shifts the position of the π-bonded phenyl proton resonances towards higher fields. The absorption in this region (δ 4.2–5.2 ppm) gave a definite evidence of a π-bonded phenyl ring in the systems. The reasons of the shift of the positions of proton resonances could be due to the combination of three factors. These are (1) the withdrawal of π-electron density from the ring by the metal, (2) the quenching of the ring currents by interaction with the metal and (3) the magnetic anisotropy of the rest of the complex.[21]

The spectra of all the other complexes which did not contain π-bonded phenyl group showed more or less identical features. The aromatic protons of the triphenylarsine, triphenylstibine and of the N-donor ligands (2,2'-bipyridine, 1,10-phenanthroline, pyridine, γ-picoline) exhibited broad resonances in the range (δ 7.0–8.5 ppm). Complexes having γ-picoline also showed a resonance band due to methyl protons around (δ 1.8–2.0 ppm).

Electronic spectra

All the complexes showed a broad medium to intense absorption band around (450–410 nm) due to the d-d or the (MLCT) transition. Generally all ruthenium(II) octahedral complexes apparently exhibit a broad envelope around 450 nm due to MLCT or/and d-d transition.[22] These results indicate an octahedral (distorted)

geometry of the donor atoms around the ruthenium(II). The geometry around metal atom in the $SnCl_3$ complexes may be considered either as distorted octahedral or tetrahedral depending upon whether C_6H_6 ring is assumed to occupy three positions or one position, respectively. We prefer the former description on the basis of the interpretation of the electronic spectral data which are similar to those of the other complexes of Ru(II) in which $SnCl_3^-$ ion is replaced by other anions. This geometry is further confirmed by the diamagnetic nature of all the complexes. In the cases of tetrahedral complexes of Ru(II) (if possible), one should expect paramagnetic behaviour due to low value of crystal field. Since the ruthenium ion is bonded with a number of π acids viz. arsine, stibine, phosphine, NO_2^-, $SnCl_3^-$, UV region showed a number of $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transition bands which have not been assigned.

On the basis of the above data a tentative structure of trichlorostannate π-bonded complexes may be proposed on the same line as that of $[RuH(PPh_3)_3]^+$ ion.[23]

In conclusion, we wish to report that in $SnCl_3$ complexes of cyclopentadienyl ruthenium(II), NO is oxidized to NO_2^- resulting in the formation of nitrito complexes. They also show evidence for the π-interaction of one of the phenyl rings of EPh_3 ligands to the ruthenium center. Further it has also been shown that a parallel nitrosylation reaction also takes place besides the formation of π-complex. The rates of the two reactions are dependant on

the nature of E in EPh_3. In phosphine complex the formation of π-complex dominates over that of nitrosylation while the contrary is true in the $SbPh_3$ complex. The rates of the reactions in the arsine complexes are competitive. The difference in the behaviour of the complexes having heterocyclic bases as coligands gives further proof for the difference in the behaviour of PPh_3, $AsPh_3$, $SbPh_3$ towards the formation of π-bonded complexes.

S.No.	Reaction Products, Colour	M.P. (^oC)	Microanalyses Found(Calcd)% C	H	N	X	IR (cm^{-1})
1	2	3	4	5	6	7	8
1.	I O	200	47.8 (48.2)	3.3 (3.6)	1.5 (1.9)	11.7 (11.0)	1870,1510,1480,14 1370,1350,1310,85 800
2.	$[Ru(NO_2)SnCl_3(PPh_3)_2]$ OR	200	49.0 (48.2)	4.2 (3.3)	2.0 (1.5)	10.5 (11.8)	1510,1480,1430,13 1350,1340,1310,85 800
3.	$[Ru(NO_2)SnCl_3(AsPh_3)_2]$ OR	204	44.1 (43.9)	4.6 (3.0)	2.1 (1.4)	10.0 (10.7)	1510,1480,1430,13 1350,1310,850,800
4.	$[Ru(NO_2)SnCl_3(SbPh_3)_2]$ OR	200	41.2 (40.1)	3.4 (2.8)	1.8 (1.3)	10.4 (9.9)	1510,1480,1430,13 1350,1320,850,800
5.	$[Ru(NO)Cl_3(AsPh_3)(Py)]$ Y	225	45.2 (44.3)	3.8 (3.2)	5.2 (4.5)	17.8 (17.0)	1860
6.	$[Ru(NO)Cl_3(AsPh_3)(\gamma\text{-Pic})]$	220	46.2 (45.2)	3.8 (3.6)	4.8 (4.3)	17.2 (16.6)	1860
7.	$[Ru(NO)Br_3(AsPh_3)(Py)]$ Y	240	37.2 (36.5)	2.8 (2.6)	4.2 (3.7)	30.8 (31.7)	1850
8.	$[Ru(NO)Br_3(AsPh_3)(\gamma\text{-Pic})]$ Y	230	37.0 (37.6)	3.2 (3.1)	3.4 (3.6)	31.4 (31.7)	1850
9.	$[Ru(NO)(NO_2)Cl_2(oPhen)]$ YB	140	34.2 (33.6)	2.2 (1.8)	12.2 (13.0)	17.4 (16.5)	1868,1520,1480,14 1380, 1320,850.

..contd.

10.	$[Ru(NO)(NO_2)Cl_2(Bipy)].\frac{1}{2}CH_2Cl_2$ YB	145	27.2 (28.0)	2.4 (2.0)	11.8 (12.4)	24.4 (23.6)	1868,1510,1480,143 1320,850
11.	$[Ru(NO)(NO_2)Br_2(OPhen)]$ B	150	27.2 (27.8)	1.4 (1.5)	9.6 (10.8)	29.8 (30.9)	1860,1520,1480,143 1380,1320,850
12.	$[Ru(NO)(NO_2)Br_2(Bipy)]$ B	148	25.2 (24.3)	2.4 (1.6)	10.8 (11.3)	31.8 (32.4)	1860,1510,1480,143 1340,1320,850
13.	$Ru(NO)(NO_2)Cl_2(SbPh_3).CH_2Cl_2$ P	132	34.2 (33.1)	2.6 (2.4)	4.4 (4.0)	19.8 (20.6)	1840,1530,1380,132 850
14.	$[Ru(NO)Cl_3(Bipy)]$ B	$>$280	31.3 (30.5)	2.4 (2.0)	10.4 (10.8)	26.2 (26.8)	1870
15.	$[Ru(NO)Cl_3(OPhen)]$ B	$>$280	34.8 (34.1)	2.2 (1.9)	10.1 (10.7)	26.2 (25.3)	1872
16.	$Ru(NO)Cl_3(SbPh_3)(Py)]$ Y	202	41.0 (41.2)	3.3 (3.0)	4.8 (4.1)	15.4 (15.8)	1840
17.	$[Ru(NO)Cl_3(SbPh_3)(\gamma\text{-Pic})]$ Y	200	42.6 (42.1)	3.6 (3.3)	4.6 (4.0)	16.2 (15.4)	1840
18.	$[RuCl_2(Py)_4]$ YB	$>$260	50.2 (49.1)	4.4 (4.0)	11.0 (11.4)	15.2 (14.5)	1600,1480,1440,107 760,700

O=Orange, OR=Orange Red, B=Brown, Y=Yellow, P=Pink, YB=Yellowish-Brown

Melting points are uncorrected.

Py = pyridine, γ-Pic = γ-Picoline, 2,2'-Bipy = 2,2'-Bipyridine, 1,10-phen = 1,10-phenanthroline.

CAPTIONS FOR THE FIGURES

Fig. 3.1 Proposed structure of the π-bonded complexes.

Infrared spectra of the complexes.

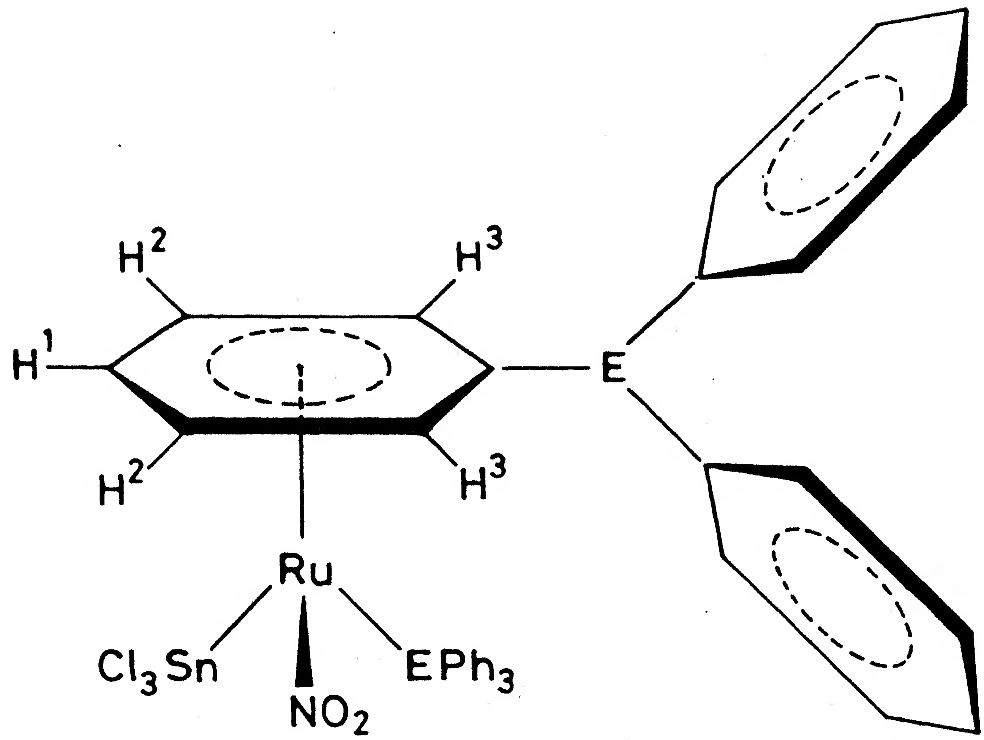
Fig. 3.2 $[Ru(NO_2)SnCl_3(AsPh_3)\{\pi\text{-}C_6H_5(AsPh_2)\}]$

Fig. 3.3 (1) $[Ru(NO)Cl_3(OPhen)]$

(2) $[Ru(NO)(NO_2)Cl_2(OPhen)]$

^1H NMR spectra of the complex.

Fig. 3.4 $[Ru(NO_2)SnCl_3(AsPh_3)\{\pi\text{-}C_6H_5(AsPh_2)\}]$



[E = P, As, Sb]

Fig. 3.1 Tentative structure of $[Ru(NO_2)(EPh_3)\{(\eta^6\text{-}C_6H_5)\ EPh_2\}(SnCl_3)]$

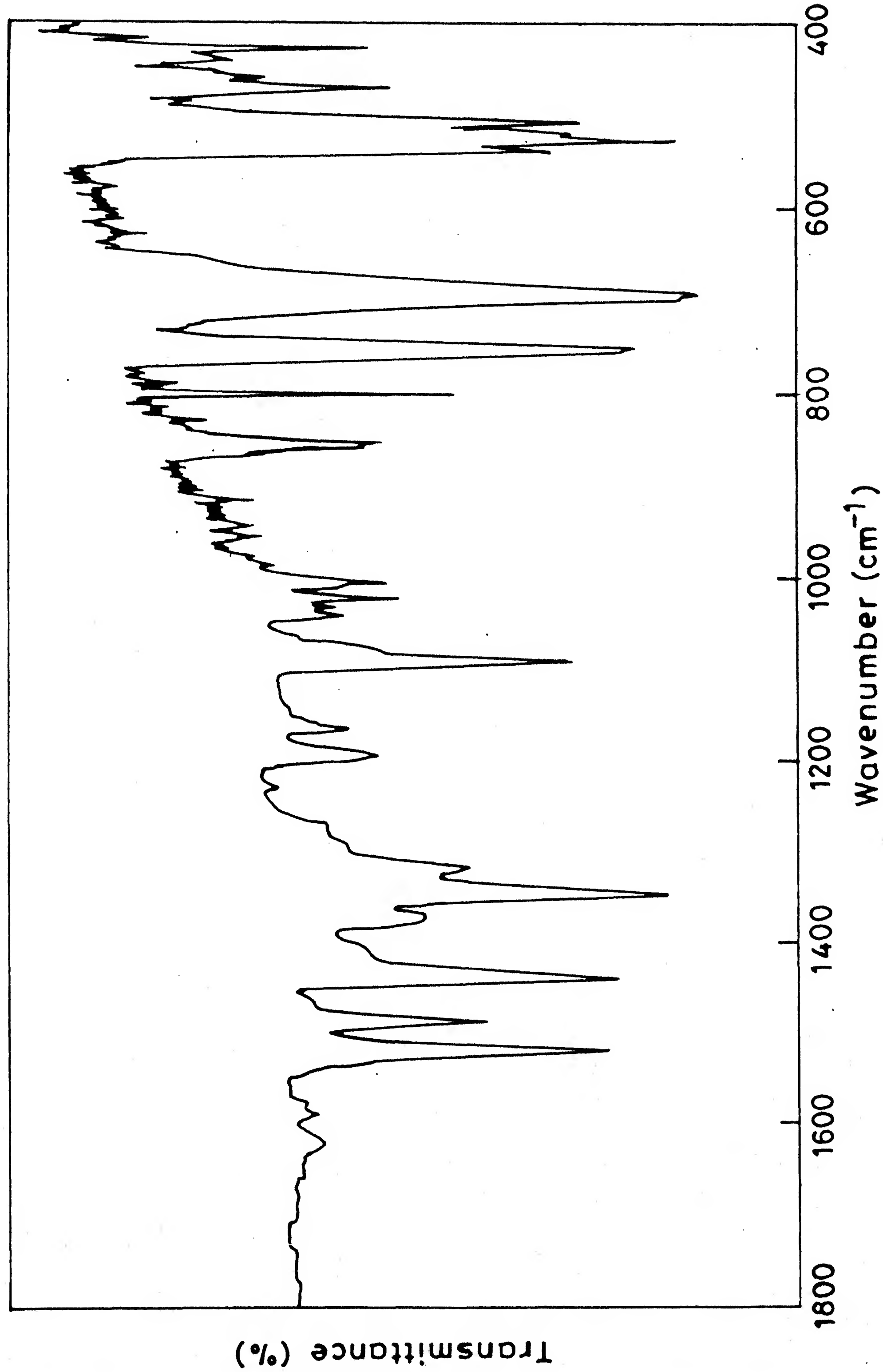


Fig. 3.2 Infrared spectrum.

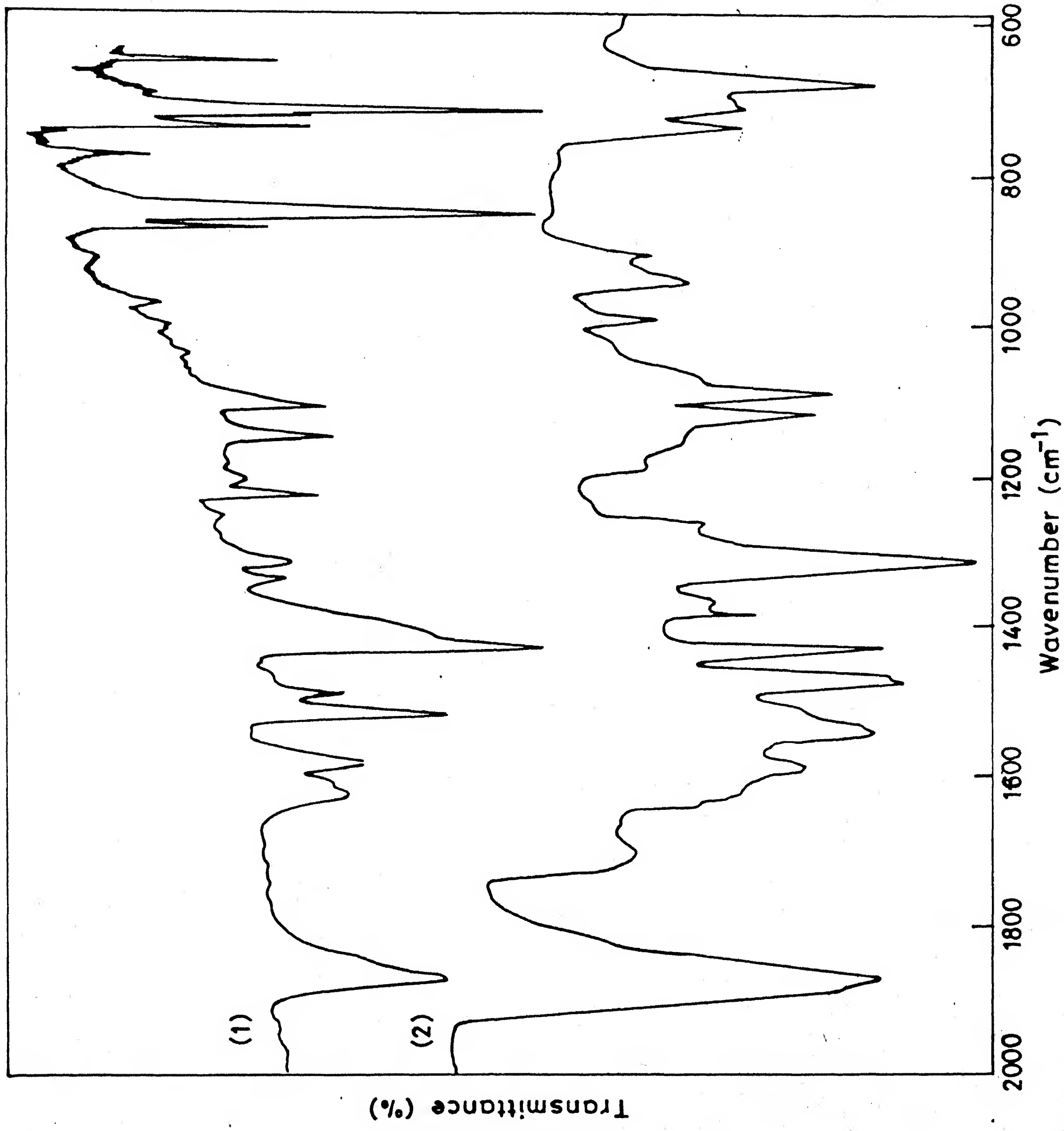


Fig. 3.3 Infrared spectra.

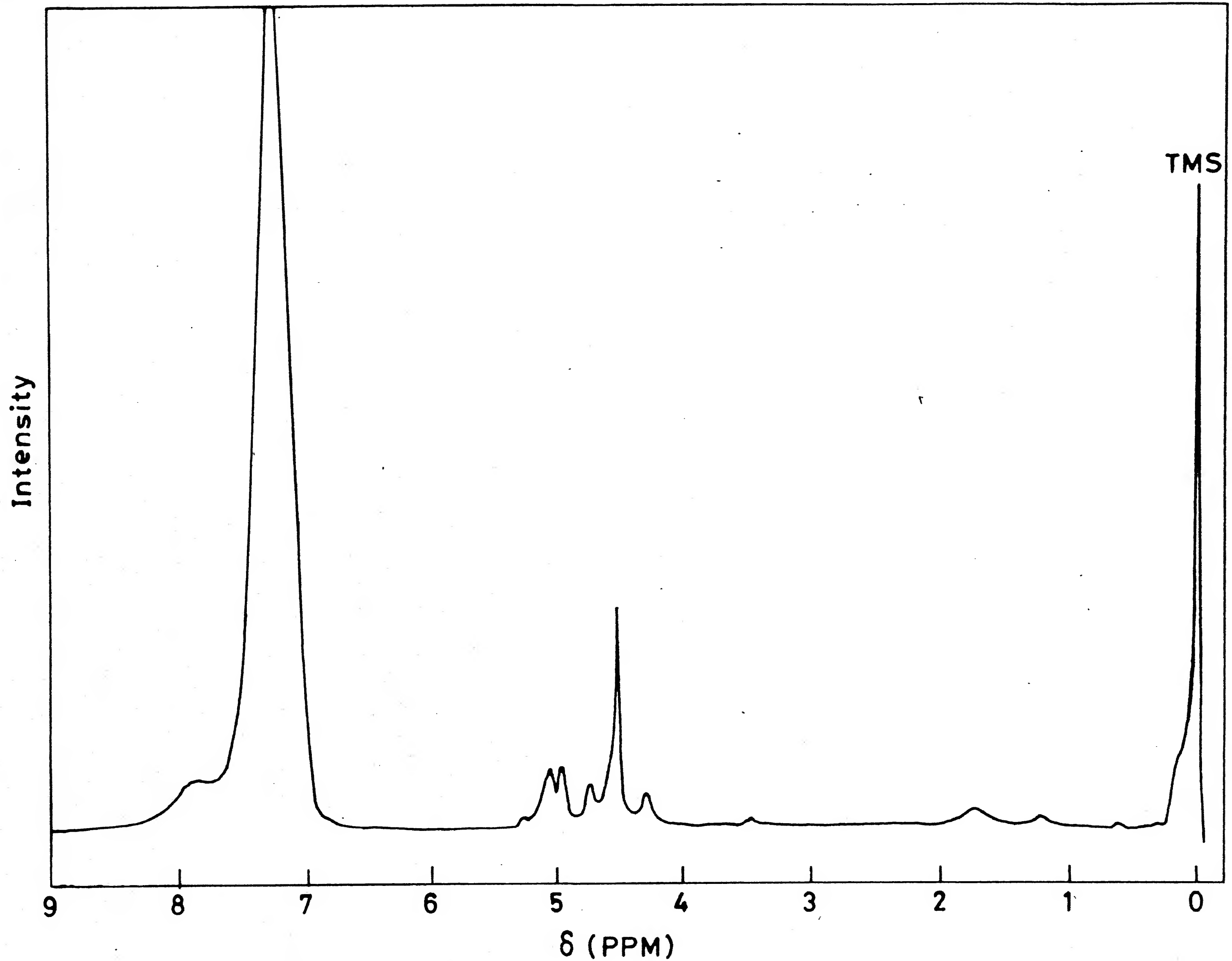


Fig. 3.4 ^1H NMR spectrum.

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Chapter - IV

Reactivity of $[RuCl_3(EPh_3)_2S]$ (E = As, P; S = DMSO, DMF, THF, CH_3CHO, CH_3CN, CS_2, $(CH_3)_2CO$) towards trithiazyl trichloride and substitution reactions of $[Ru(NS)Cl_3(EPh_3)(E'Ph_3)]$ (E = As, P; E'=As, P,Sb)

4.1 Introduction

Trithiazyl trichloride, $N_3S_3Cl_3$ is air sensitive and unstable in different solvents. It is well established that depending upon the reaction conditions it interacts with metal salts or complexes affording various interesting products containing NS^+, N_2S_2, $N_2S_2^{2-}$, $N_3S_2^{2-}$, $NSCl^{2-}$, NSCl, etc. as coligands.[1-7] Although attention has been drawn to the use of NSCl as a synthetic potential for metal thionitrosyls, yet all attempts have been plagued by problems of the still undefined reaction conditions, under which it is able to act as a thionitrosylating agent. No suggestion has yet been made in this direction. The problem is, therefore, still in an embroynic state. For want of the reaction conditions

and for our interest in the ligand exchange reactions as potential synthetic approach for metal thionitrosyls, we have decided to react $N_3S_3Cl_3$ with ruthenium complexes having coordinated solvent molecules. Besides, a study of ligand substitution reactions of $[Ru(NS)Cl_3(EPh_3)_2]$ and $[Ru(NS)Cl_3(EPh_3)(E'Ph_3)]$ with $E''Ph_3$ (E'' = P, As, Sb) and N-donor heterocyclic bases were also carried out. This chapter describes a few reactions in this direction.

4.2 Experimental

All the chemicals used were of Analar or chemically pure grade. Solvents were dried prior to use by the conventional methods.[10] Trithiazyltrichloride, $[RuCl_3(EPh_3)_2S]$ were prepared by the literature methods.[8,9]

(A) Preparation of Complexes

1. Reactions of $N_3S_3Cl_3$ with $[RuCl_3(EPh_3)_2S]$ (E = P, As; S = CH_3CHO, DMF, DMSO, THF, CH_3CN, CS_2, $(CH_3)_2CO$)

A typical reaction has been carried out as under:

A saturated mint green solution of trithiazyl trichloride in THF (10 ml) was added with stirring to a solution of $[RuCl_3-(EPh_3)_2S]$ (*ca.* 0.26 mmol) in 40 ml of dichloromethane. The

stirring was continued for an hour. A red coloured solution was obtained; 50 ml of methanol was added to it, followed by the addition of an excess of ligand EPh_3 (E = P, As, Sb) (ca. 0.04 mmol) whereupon a brown microcrystalline compound was obtained. It was separated by centrifugation, washed with methanol, water, methanol and finally with ether and dried under vacuo (yield, ca 60%). The analytical data corresponded with the formula given in Table 4.1.

The same compounds $[Ru(NS)Cl_3(EPh_3)_2]$ were also obtained, though in low yields, using zinc as reducing agent≠ in place of the EPh_3.

(2) Reactions of $[Ru(NS)Cl_3(EPh_3)(E'Ph_3)]$ with $E''Ph_3$ (E = P, As; E' = P, As, Sb; E'' = P, As, Sb)

The reactions were carried out by the following general procedure. The details and conditions of the reactions are given in Table 4.2.

A solution of $[Ru(NS)Cl_3(EPh_3)(E'Ph_3)]$ (1 mmol) and $E''Ph_3$ (5 mmol) in 50 ml of chloroform was refluxed for a few hours

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≠ In the reactions of $[RuCl_3(EPh_3)_2S]$ (S = DMSO, DMF, CS_2) with $N_3S_3Cl_3$, the solution obtained after stirring and zinc reduction yielded $[Ru(NS)Cl_3(EPh_3)_2]$ as a precipitate in a very low yield. From the filtrate, after its concentration, a black compound was obtained which was not characterized.

(cf. Table 4.2). The solution, thus obtained, was concentrated to about 10 ml. Addition of 50 ml of methanol to the concentrate yielded shining brown crystals of [$Ru(NS)Cl_3(EPh_3)(E''Ph_3)$] or [$Ru(NS)Cl_3(E''Ph_3(E''Ph_3)$],which were separated by centrifugation, washed with methanol, water, methanol, ether and dried under vacuum (yield, <u>ca</u> 80%).

(3) <u>Reactions of [$Ru(NS)Cl_3(EPh_3)(E'Ph_3)$] with heterocyclic bases L (L = pyridine, γ-picoline, pyrazine, pyrazole)</u>

(a) [$Ru(NS)Cl_3(EPh_3)(E'Ph_3)$] (<u>ca</u>. 0.14 mmol) in 40 ml of chloroform was refluxed with the heterocyclic base (<u>ca</u>. 0.4 mmol) for a few hours (cf. Table 4.3) whereby the colour of the solution was changed from orange to red-brown. The resulting solution was concentrated to about 10 ml. The addition of petroleum ether (40–60^{o}) to the concentrate yielded a compound which was separated. It was recrystallised 2–3 times from benzene/petroleum ether (40–60^{o}).

(b) A solution of [$Ru(NS)Cl_3(EPh_3)(E'Ph_3)$] (ca. 0.12 mmol) and base (ca. 0.7 mmol) in 40 ml of chloroform was refluxed for a few hours. The resulting solution was concentrated to nearly half its volume, followed by the addition of n-hexane whereby a compound was precipitated. It was separated, thoroughly washed with benzene, ether and recrystallised several times with dichloromethane/hexane.

The reactions described in section (3) were also carried out in benzene yielding the same compounds.

(B) Measurements

The melting points of the complexes were determined on the Fisher-Johns apparatus. Infra-red spectra of the complexes were recorded using Perkin Elmer Model 580 spectrometer in the range 4000-200 cm^{-1}. The samples were prepared as KBr discs. Electronic spectra were recorded on Cary 17-D spectrometer. ^{31}P NMR were recorded on Bruker WM 400 MHz in $CDCl_3$ (with external reference 85% H_3PO_4). The analyses of the complexes for halogens sulphur were carried out as reported elsewhere.[10] C, H and N were estimated by the Microanalytical laboratory of the I.I.T. Kanpur, India.

4.3 Results and Discussion

The reactions of $N_3S_3Cl_3$ with $RuCl_3(EPh_3)_2S$ (S = CH_3CHO, DMSO, DMF, THF, $(CH_3)_2CO$, CS_2, CH_3CN) yielded yellowish-brown complexes whose microanalytical data suggested the formula $[Ru(NS)Cl_3(EPh_3)_2]$. The purity of the compounds was tested by tlc. These compounds, being synthesized previously[11] by different routes have been confirmed by comparing the list of physical data with those of the authentic samples. Thus, these compounds are brown, diamagnetic solids, freely soluble in dichloromethane and

other organic solvents to give dark brown solutions. Their mp, mixed mp, X-ray powder pattern data matched exactly with those of the authentic samples. These conclusions were further supported by (1) their ir spectra which displayed the expected band around 1310 cm^{-1} attributable to terminal $(NS)^+$ group besides the characteristic bands of EPh_3 (E = P, As, Sb) and by (2) ^{31}P nmr data which exhibited phosphorus resonance at δ 13.3 ppm similar to that found in literature complex.

These reactions appeared to be slightly complicated and perhaps proceeds with an intermediate formation. All efforts to isolate the intermediate in the pure solid form were unsuccessful. Although the solutions, obtained after the initial $N_3S_3Cl_3$ reactions with ruthenium complexes yielded a precipitate with light petroleum ether but it became oily on purifying it through reprecipitation and drying. Possibly a coordinatively unsaturated Ru(III) complex is initially formed as an intermediate followed by its reduction with the formation of coordinatively saturated complex by linking with the ligand $E''Ph_3$.

$$[RuCl_3(EPh_3)(E'Ph_3)S] \xrightarrow[THF]{N_3S_3Cl_3} [RuCl_3(EPh_3)(E'Ph_3)NSCl] + S$$

$$\downarrow$$

$$[RuCl_3EPh_3\ NSCl] + E'Ph_3$$

$$\downarrow \quad E''Ph_3$$

$$[Ru(NS)Cl_3(EPh_3)(E''Ph_3)]$$

(yield, ~80%)

$$[RuCl_3(EPh_3)(E'Ph_3)S] \xrightarrow[THF]{N_3S_3Cl_3} [RuCl_3(EPh_3)(E'Ph_3)NSCl] + S$$

$$\downarrow$$

$$[RuCl_3(EPh_3)\ NSCl] + E'Ph_3$$

$$\downarrow \quad Zn$$

$$[Ru(NS)Cl_3(EPh_3)(E'Ph_3)]$$

(low yield)

Substitution reactions of $[Ru(NS)Cl_3(EPh_3)(E'Ph_3)]$ with $E''Ph_3$ (E = P, As; E' = P, As, Sb; E'' = P, As, Sb) led to the formation of $[Ru(NS)Cl_3(EPh_3)(E''Ph_3)]$ or $[Ru(NS)Cl_3(E'Ph_3)-(E''Ph_3)]$. These compounds exhibited similar analytical, spectral (ir, ^{31}P nmr, etc) data and similar chemical and physical properties as those of earlier literature known complexes synthesized by photochemical process.[11] It suggested that these complexes are the substituted derivatives of $[Ru(NS)Cl_3(EPh_3)_2]$.

A chemically interesting feature of these reactions is the fact that the variation in the reaction rates of $[Ru(NS)Cl_3(EPh_3)-(E'Ph_3)]$ with $E''Ph_3$ (E'' = P, As, Sb) is in the order $PPh_3 < AsPh_3 < SbPh_3$. The reaction of $[Ru(NS)Cl_3(PPh_3)_2]$ with $AsPh_3$ resulted in the formation of $[Ru(NS)Cl_3(AsPh_3)_2]$ in 48 hours, whereas the reverse process with PPh_3 takes only 2 hrs, and that of $[Ru(NS)Cl_3(AsPh_3)(SbPh_3)]$ with $SbPh_3$ did not yield $[Ru(NS)Cl_3(SbPh_3)_2]$ even after a longer refluxing period. The reason for the variation in rates could be due to the difference in σ-basic and π-acidic characters of the ligands ($PPh_3 > AsPh_3 > SbPh_3$). The stability of the complexes were in the order $PPh_3 > AsPh_3 > SbPh_3$ as reported elsewhere.[13] Owing to the weak π-acidic nature of As followed by that of Sb, the Ru-As and Ru-Sb bonds should be relatively weaker compared to that of Ru-P thus suggesting the order of the ligands substitution rate as $PPh_3 < AsPh_3 < SbPh_3$. Another point of importance in the lability of the Ru-EPh_3 (E = P, As or Sb) bonds could be that of steric hindrance or the trans effect. For PPh_3 the space-filling

model suggested that the second PPh_3 molecule in $[Ru(NS)Cl_3(PPh_3)_2]$ should be quite labile due to steric compression.

Substitution reactions of $[Ru(NS)Cl_3(EPh_3)(E'Ph_3)]$ with the heterocyclic bases (L), viz. pyridine, γ-picoline, pyrazine, pyrazole led to the formation of $[Ru(NS)Cl_3(EPh_3)L]$ or $[Ru(NS)Cl_3-(E'Ph_3)L]$. The ir spectra of these complexes, exhibited bands due to vibrational modes of bases, viz. pyridine (1590, 1580, 1440, 1218, 1148, 1080, 735 cm^{-1}), γ-picoline (1600, 1505, 820, 730–720 cm^{-1}), pyrazine (1400–1370, 1238, 1148, 1118, 1022, 800 cm^{-1}) or pyrazole (3080, 1560, 1470, 1360, 1130 cm^{-1}) besides the bands due to $(\nu_{NS})^+$ around 1310 cm^{-1} and characteristic bands of EPh_3. The moderately intense band around 320-290 cm^{-1} was assigned to (ν_{Ru-Cl}).

The substitution reactions of $[Ru(NS)Cl_3(EPh_3)(E'Ph_3)]$ with bases like 2,2'-bipyridine, and 1,10-phenanthroline failed. Inspite o the change of solvents and the time of reactions, these reactions like others did not proceed. In all the cases these reactions led to the formation of a mixture of products. Attempts to separate them were unsuccessful. The presence of different products were confirmed by ^{31}P nmr which displayed a number of bands. Efforts to synthesize bridged compounds with pyrazine were also unsuccessful and only monomers have been obtained.

The substitution of one PPh_3 molecule by heterocyclic base molecule depleted electron density at the ruthenium center through $d_\pi - d_\pi$ back bonding. As a consequence electron density available

at ruthenium for $d_\pi - d_\pi$ back bonding towards the remaining PPh_3 molecule is reduced. This results in the reduction of net electron density at phosphorus causing a downfield shift from (δ 13 to 25 ppm) depending upon the nature of heterocyclic molecule attached to ruthenium. Moreover, if it is assumed that both phosphine molecules are trans to each other in $[Ru(NS)Cl_3(PPh_3)_2]$, replacement of one PPh_3 by heterocyclic base will lower the trans effect (trans effect of PPh_3 is greater than that of base)[15] thereby strengthening the Ru–P bond by sigma bond formation. Thus formation of stronger P $\longrightarrow$ Ru σ bond and weaker Ru $\longrightarrow$ P π back bonding will result in the lower electron density at P and will cause the observed downfield shift.

The visible spectra of all the complexes exhibited a rather broad band around 450 nm. Since it is generally believed that (MLCT) transition in ruthenium(II) octahedral complexes occur under a broad band around 450–430 nm[16], a similar band in the electronic spectra of our complexes suggested octahedral geometry around Ru(II) ions. The electronic spectra of the starting complexes $[RuCl_3(EPh_3)_2S]$ showed bands in the region 620–350 nm.

The intraligand bands due to triphenylphosphine, triphenylarsine, triphenylstibine, pyridine, γ-picoline, pyrazine, pyrazole in the region around 330–260 nm were also observed.

All the complexes were found to be diamagnetic suggesting ruthenium in +2 oxidation state having (d^6) system. It is therefore

suggested that the reactions of $RuCl_3(EPh_3)_2S$ with thiazylchloride resulted in the formation of $[Ru(NS)Cl_3(EPh_3)(E'Ph_3)]$, which on further reaction with $E''Ph_3$ and N-donor heterocyclic bases [L], led to the formation of $[Ru(NS)Cl_3(EPh_3)(E''Ph_3)]$ and $[Ru(NS)Cl_3$-$(EPh_3)L]$.

Table 4.1. Thionitrosyl complexes of Ru(II), characterisation data of complexes

S.No.	Reactant	Ligand	Product Colour, M.P. (^{o}C)	Analyses: Found (Calcd)% C	H	N	X	S	IR(NS)$^{+}$ cm^{-1}
1.	$[RuCl_3(PPh_3)_2S]$	PPh_3	$Ru(NS)Cl_3(PPh_3)_2$ B 176	56.2 (55.6)	3.6 (3.9)	1.8 (1.8)	13.4 (13.7)	4.8 (4.1)	1316
2.	$[RuCl_3(AsPh_3)_2S]$	$AsPh_3$	$Ru(NS)Cl_3(AsPh_3)_2$ B >280	49.0 (49.9)	3.8 (3.4)	1.2 (1.6)	12.4 (12.3)	3.4 (3.8)	1310
3.	$[RuCl_3(PPh_3)_2S]$	$AsPh_3$	$Ru(NS)Cl_3(PPh_3)(AsPh_3)$ B 245-7	52.1 (52.6)	3.0 (3.7)	2.2 (1.6)	13.4 (12.9)	3.6 (4.0)	1305
4.	$[RuCl_3(AsPh_3)_2S]$	$SbPh_3$	$Ru(NS)Cl_3(AsPh_3)(SbPh_3)$ B 220	47.1 (47.4)	3.5 (3.3)	1.6 (1.5)	11.8 (11.6)	3.4 (3.6)	1300

Colour B = Brown

S = CH_3CHO, DMF, DMSO, THF, $(CH_3)_2CO$, CH_3CN, CS_2.

Table 4.2. Procedure for ligand substitution in thionitrosyl complexes

S.No.	Reactant	Ligand ($E''Ph_3$)	Time for refluxing (h)	Solvent	Product
1.	$[Ru(NS)Cl_3(AsPh_3)(PPh_3)]$	PPh_3	1	$CHCl_3$	$[Ru(NS)Cl_3(PPh_3)_2]$
2.	$[Ru(NS)Cl_3(PPh_3)_2]$	$AsPh_3$	8	$CHCl_3$	$[Ru(NS)Cl_3(PPh_3)(AsPh_3)]$
3.	$[Ru(NS)Cl_3(AsPh_3)_2]$	PPh_3	2	$CHCl_3$	$[Ru(NS)Cl_3(PPh_3)_2]$
4.	$[Ru(NS)Cl_3(AsPh_3)(PPh_3)]$	$AsPh_3$	48	$CHCl_3$	$[Ru(NS)Cl_3(AsPh_3)_2]$
5.	$[Ru(NS)Cl_3(AsPh_3)(SbPh_3)]$	$AsPh_3$	3	$CHCl_3$	$[Ru(NS)Cl_3(AsPh_3)_2]$
6.	$[Ru(NS)Cl_3(AsPh_3)(SbPh_3)]$	PPh_3	1	$CHCl_3$	$[Ru(NS)Cl_3(AsPh_3)(PPh_3)]$
7.	$[Ru(NS)Cl_3(AsPh_3)(SbPh_3)]$	$SbPh_3$	72	$CHCl_3$	Mixture of Products
8.	$[Ru(NS)Cl_3(PPh_3)_2]$	$SbPh_3$	72	$CHCl_3$	Mixture of Products

E'' = P, As, Sb

e 4.3. Characteristic data of the Reactions of $[Ru(NS)Cl_3(EPh_3)(E'Ph_3)]$ with heterocyclic ligands

Reactant	Base	Procedure (C) Time for reflux	Product M.P.* (^oC), Colour	Analyses: Found(Calcd)% C	H	N	X	S	IR $(NS)^+$ cm^{-1}
2	3	4	5	6					7
$[Ru(NS)Cl_3(PPh_3)_2]$	Py	2, (i)	$[Ru(NS)Cl_3(PPh_3)(Py)]$ Y 128	46.1 (46.4)	4.3 (3.4)	5.4 (4.7)	17.1 (17.8)	4.9 (5.3)	1310
$[Ru(NS)Cl_3(PPh_3)_2]$	γ-Pic	2, (i)	$[Ru(NS)Cl_3(PPh_3)(\gamma\text{-Pic})]$ Y 125	47.8 (47.4)	4.1 (3.7)	5.2 (4.6)	17.7 (17.4)	5.0 (5.2)	1310
$[Ru(NS)Cl_3(PPh_3)_2]$	Pz	3, (ii)	$[Ru(NS)Cl_3(PPh_3)(Pz)]$ B 195	44.9 (44.3)	3.6 (3.1)	6.8 (7.0)	17.6 (17.8)	4.8 (5.3)	1300
$[Ru(NS)Cl_3(PPh_3)_2]$	Pa	3, (i)	$[Ru(NS)Cl_3(PPh_3)(Pa)]$ Y 140	43.9 (43.2)	3.8 (3.2)	7.7 (7.2)	18.4 (18.1)	5.2 (5.4)	1310
$[Ru(NS)Cl_3(AsPh_3)_2]$	Py	3, (i)	$[Ru(NS)Cl_3(AsPh_3)(Py)]$ Y 125-8	42.8 (43.2)	3.2 (3.1)	4.8 (4.3)	17.0 (16.6)	5.4 (5.0)	1310
$[Ru(NS)Cl_3(AsPh_3)_2]$	γ-Pic	3, (i)	$[Ru(NS)Cl_3(AsPh_3)(\gamma\text{-Pic})]$ Y 125	44.9 (44.1)	4.1 (3.5)	5.1 (4.3)	16.8 (16.2)	5.2 (4.9)	1310
$[Ru(NS)Cl_3(AsPh_3)_2]$	Pz	12, (ii)	$[Ru(NS)Cl_3(AsPh_3)(Pz)]$ B 280	40.9 (41.3)	3.4 (3.0)	6.4 (6.5)	17.2 (16.5)	5.0 (5.1)	1320
$[Ru(NS)Cl_3(AsPh_3)_2]$	Pa	6, (ii)	$[Ru(NS)Cl_3(AsPh_3)(Pa)]^e$ B 175-8	40.9 (40.1)	3.2 (3.3)	6.8 (6.5)	17.2 (16.9)	5.5 (5.1)	1310

...contd.

Table 4.3 (contd.)

1	2	3	4	5	6	7
9.	[Ru(NS)Cl_3($AsPh_3$)($SbPh_3$)]	Pa	5, (ii)	[Ru(NS)Cl_3($SbPh_3$)(Pa)] G 145	38.2 3.4 6.2 16.2 52. (37.4) (2.9) (6.5) (15.7) (4.7)	1310
10.	[Ru(NS)Cl_3($AsPh_3$)($SbPh_3$)]	Py	3, (i)	[Ru(NS)Cl_3)(Py)] Y 128-30	41.2 3.2 4.4 16.1 4.4 (40.2) (2.9) (4.0) (15.4) (4.0)	1310
11.	[Ru(NS)Cl_3($AsPh_3$)($SbPh_3$)	γ-Pic	3, (i)	[Ru(NS)Cl_3($SbPh_3$)(γ-Pic)] Y 125	42.2 3.4 4.4 15.8 5.3 (41.2) (3.2) (4.1) (15.1) (4.6)	1310
12.	[Ru(NS)Cl_3($AsPh_3$)(PPh_3)]	Py	3, (i)	[Ru(NS)Cl_3($AsPh_3$)(Py)] Y 128	46.8 3.8 5.1 17.2 5.8 (46.4) (3.4) (4.7) (17.8) (5.3)	1310
13.	[Ru(NS)Cl_3($AsPh_3$)(PPh_3)]	γ-Pic	3, (i)	[Ru(NS)Cl_3($AsPh_3$)(γ-Pic)] Y 125	47.2 3.2 5.2 16.8 5.4 (47.4) (3.7) (4.6) (17.4) (5.2)	1310
14.	[Ru(NS)Cl_3($AsPh_3$)(PPh_3)]	Pa	4, (i)	[Ru(NS)Cl_3($AsPh_3$)(Pa)] B 175	43.2 3.8 7.4 17.4 5.8 (43.9) (3.2) (7.2) (18.1) (5.4)	1310

*M.P. are uncorrected

B=Brown, Y=Yellow, G=Green

Py=pyridine, γ-Pic= γ-Picoline, Pa=pyrazole, Pz=pyrazine

e=Mass spectra(FD) Found 624 calculated 627 (Joel - 015G-2FD)

CAPTIONS FOR THE FIGURES

Infrared spectra of the complexes.

Fig. 4.1 $[Ru(NS)Cl_3(AsPh_3)_2]$

Fig. 4.2 (a) $[Ru(NS)Cl_3(AsPh_3)(py)]$

(b) $[Ru(NS)Cl_3(PPh_3)(\gamma\text{-pic})]$

(c) $[Ru(NS)Cl_3(PPh_3)(pa)]$

^{31}P NMR spectra of the complexes

Fig. 4.3 (a) $[Ru(NS)Cl_3(PPh_3)_2]$

(b) $[Ru(NS)Cl_3(PPh_3)(py)]$

(c) $[Ru(NS)Cl_3(PPh_3)(pa)]$

(d) $[Ru(NS)Cl_3(PPh_3)(pz)]$

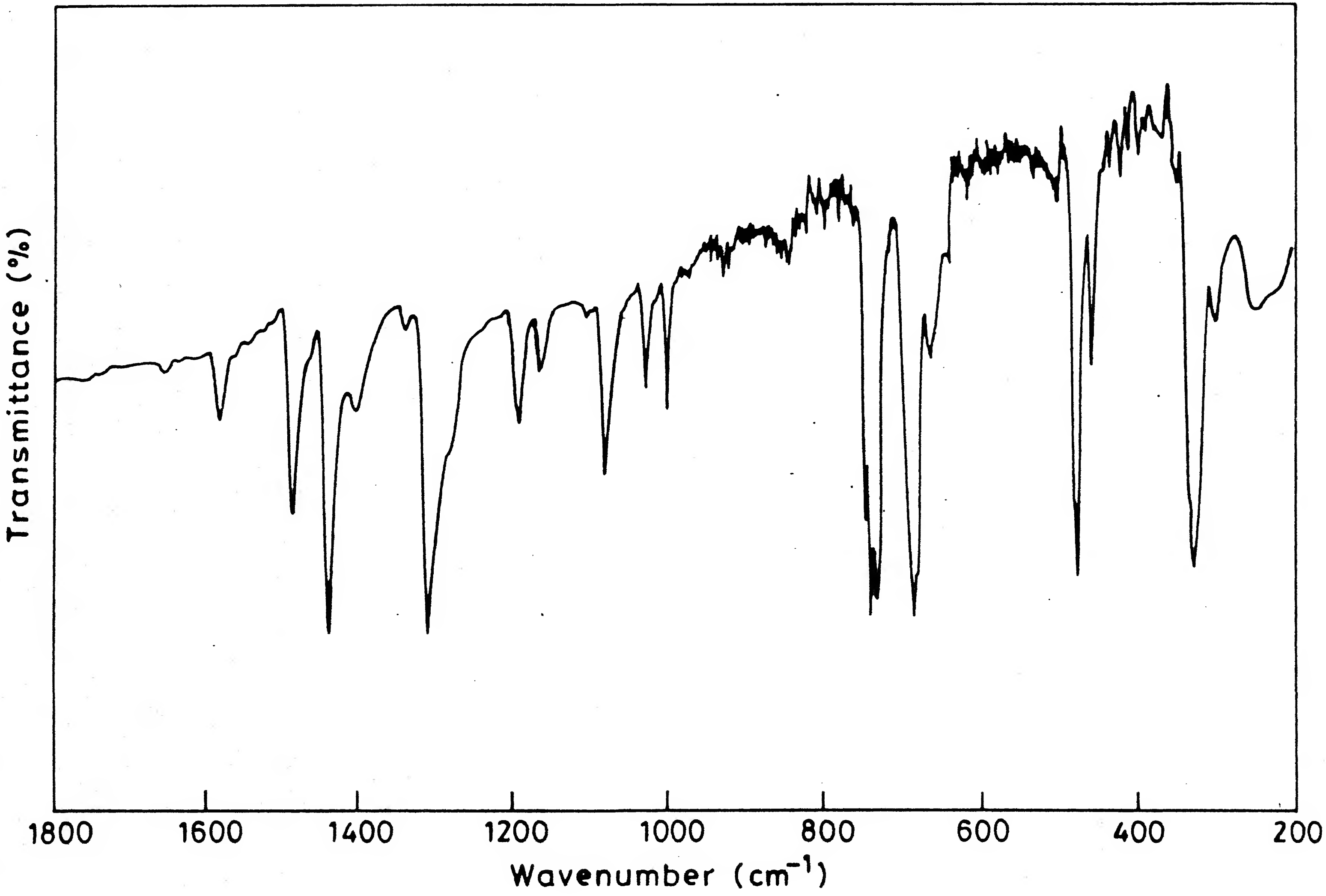

Fig. 4.1 Infrared spectrum.

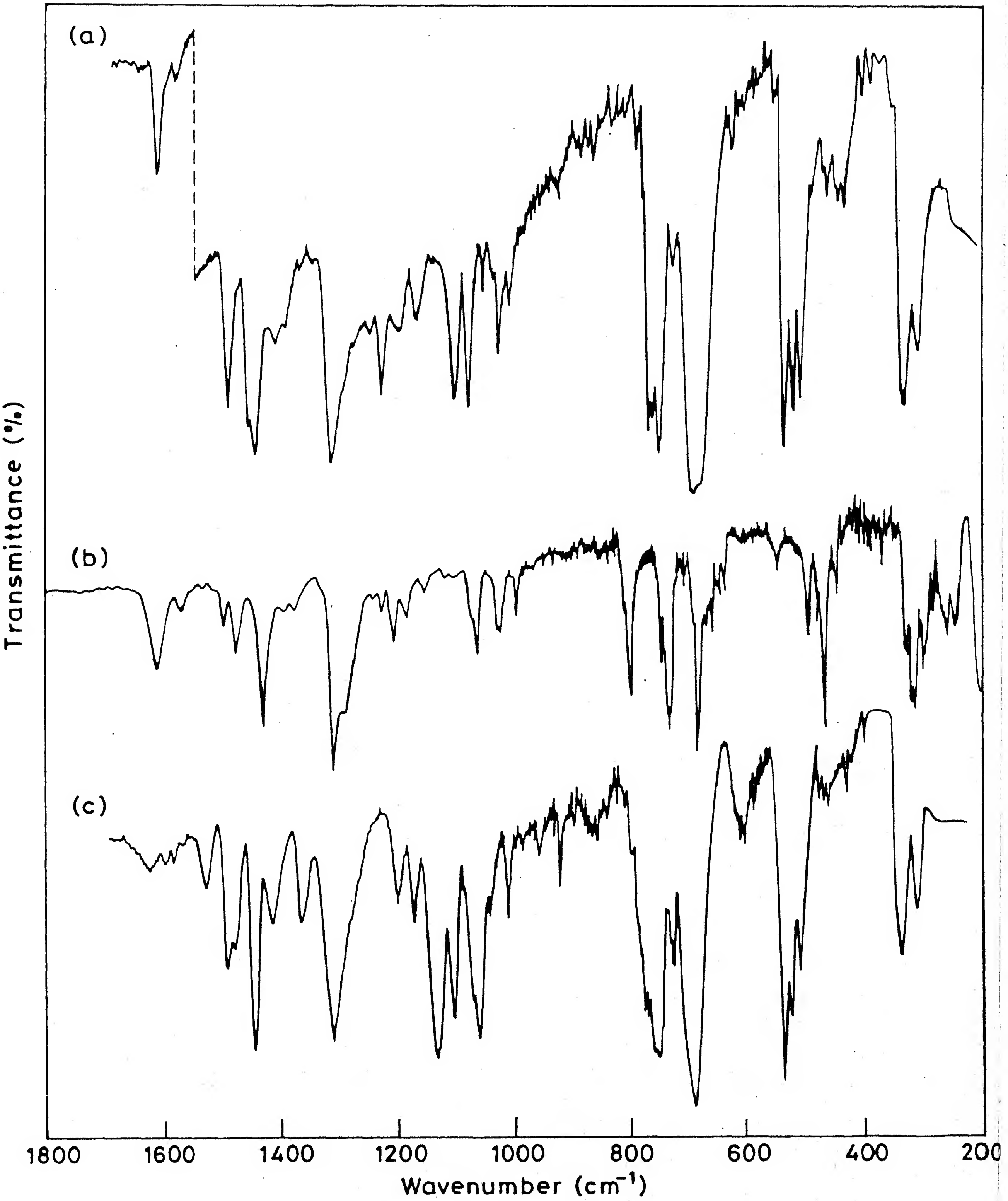

Fig. 4.2 Infrared spectra.

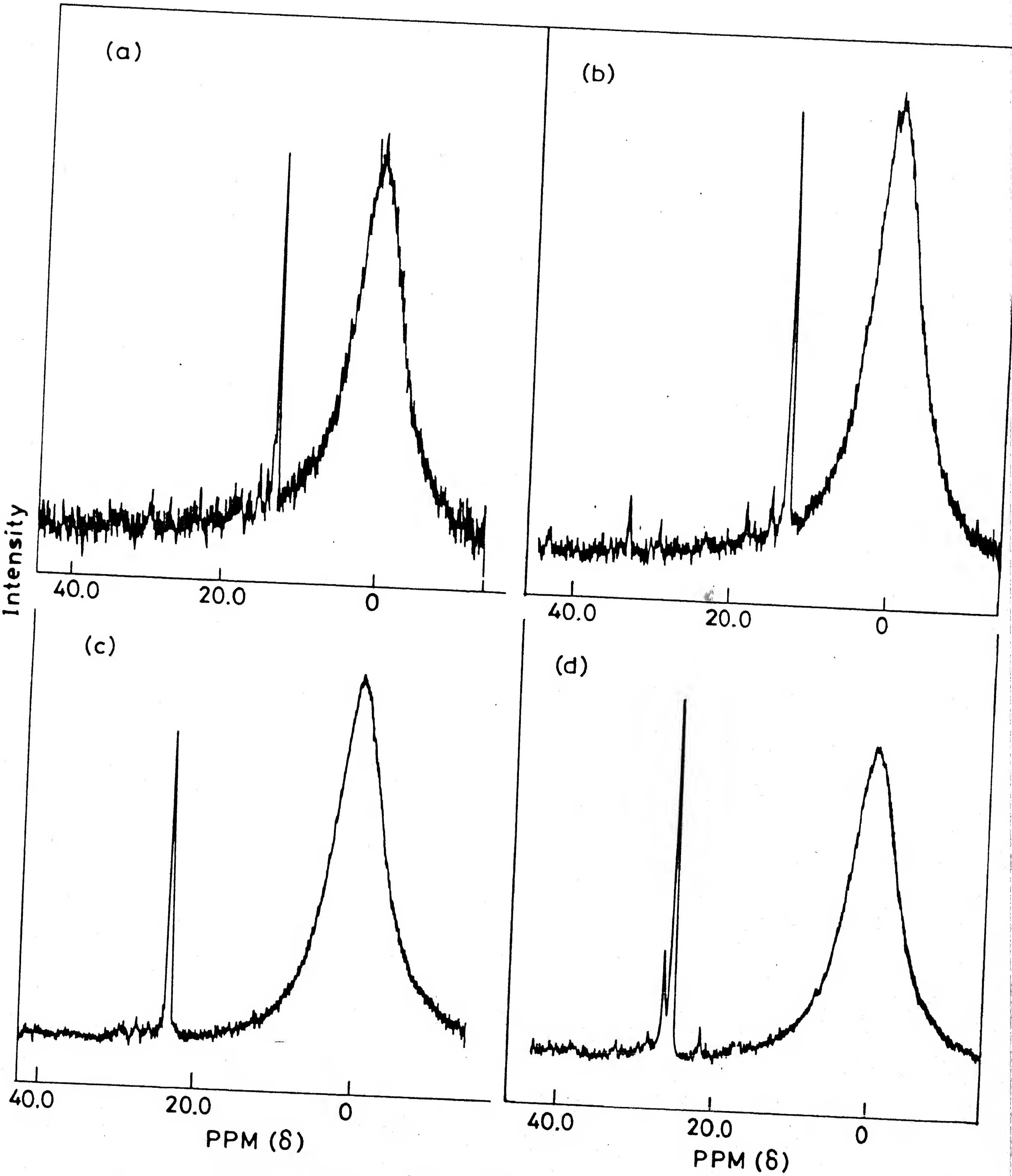

Fig. 4.3 ^{31}P NMR spectra.

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Chapter – V

Reactions of EPh_3 (E = P, As) with coordinated NS group of $[Ru(NS)Cl_3(EPh_3)_2]$ in different solvents

5.1 Introduction

Difficulties in the synthetic area of thionitrosyl complexes have been largely due to non-availability of monomeric NS radical which has only a transient existance and gets polymerized into a number of products. During the past several years it has been established that NS radical is stabilized by coordination to transition metal ions. Although a number of metals (Cr, Mo, W, Mn, Tc, Re, Ru, Os, Co) form thionitrosyl complexes,[1,2] the literature survey indicates no work regarding the reactions of coordinated NS with various nucleophiles and electrophiles. Such reactions will make an interesting study because of our belief that the behaviour of these reactions will be entirely different in relation to those of metal nitrosyls. Though the progress in

this direction will be a slow one, due to the difficulty in structural characterization of the products, an initiative is, however warranted for an understanding of the complicated chemistry of sulphur-nitrogen ligands. The reactions between $[Ru(NS)Cl_3(EPh_3)(E'Ph_3)]$ (E = P, As; E' = P, As, Sb) and EPh_3 (E = P, As) were considered with a view to study the nucleophilic attack of EPh_3 on the sulphur (electrophile) of the bonded NS group in benzene and other non-coordinating solvents. The results of a study of these reactions have been presented in this chapter.

5.2 Experimental

The chemicals used were of Analar grade. Solvents were dried and distilled before use. The complexes $[Ru(NS)Cl_3(EPh_3)(E'Ph_3)]$ were prepared and purified by the literature methods. Carbon, hydrogen and nitrogen were analysed by the Microanalytical Laboratory of the Indian Institute of Technology, Kanpur, India. Sulphur and halogens were estimated as reported in the literature.[4] Melting points were recorded on Fisher-johns melting point apparatus and are uncorrected. The electronic spectra of the complexes in dichloromethane solution were recorded on Cary 17-D model spectrometer. Infra-red spectra of the complexes were recorded with a Perkin-Elmer model 580 spectrometer in the 4000-200 cm^{-1} and the samples were prepared as KBr discs. ^{31}P NMR were recorded on Bruker WM-400 MHz NMR spectrometer ^{1}H NMR were recorded

on WP-80 spectrometer. Magnetic moments were measured, by the Gouy method using $Hg[Co(NCS)_4]$ as the calibrant. The EPR measurements were made on a Varian E 109X band spectrometer.

(A) Preparation of Complexes

(1) Effect of Refluxing of $[Ru(NS)Cl_3(PPh_3)_2$ in different solvents (Benzene, Toluene, Chloroform, Xylene)

(A) A solution of $[Ru(NS)Cl_3(PPh_3)_2]$ (0.2mmol)in 30 ml of solvent was heated to reflux for 2-3 hours whereby a dark brown micro-crystalline compound [I] appeared. It was separated by filtration, washed a number of times with dichloromethane, methanol, ether and dried under vacuum and analysed (yield, ca, 40%). MP = $>280^oC$ (Found: C, 50.0; H, 4.2; N, 3.0; Cl, 17.0; S, 4.8. Calcd. for $[RuN_2S_2Cl_6(PPh_3)_3]$: C, 50.1; H, 3.5; N, 2.1; Cl, 16.5; S, 4.9, IR: in addition to bands due to PPh_3, $(\nu_{NS})^+$ = 1290 cm^{-1}.

The filtrate was evaporated to 10 ml at reduced pressure, followed by the addition of petroleum ether (40-60^o), whereupon a brown microcrystalline product (II) was obtained. It was washed with methanol, water, methanol, ether and dried. (Found: C, 56.1; H, 4.4; N, 2.0; Cl, 13.8; S, 3.6, Calc. for $[Ru(NS)Cl_3(PPh_3)_2]$ C, 55.7; H, 3.8; N, 1.8; Cl, 13.6; S, 4.1, IR: $(\nu_{NS})^+$ = 1316 cm^{-1}, ^{31}P = δ 13.3 ppm, mp. = 176^oC.

(B) A solution of $[Ru(NS)Cl_3(PPh_3)_2]$(0.1mmol) in 20 ml of benzene was refluxed for eight hours whereby a dark brown compound appeared. It was separated and washed with dichloromethane, methanol, ether and dried. M.P. $> 280^{o}C$. IR: $(\nu_{NS})^+ = 1290\ cm^{-1}$ (broad), 1120 cm^{-1} (Found: C, 45.2; H, 4.3; N, 5.4).

(C) A solution of $[Ru(NS)Cl_3(PPh_3)_2]$(0.1mmol) in 20 ml of benzene or toluene was refluxed for 2-3 days. An insoluble brownish product was crystallised out of solution which was separated and analysed. It appeared to be a mixture containing two products, one of products appeared to be the brown compound (I) and the other is compound (IV) (vide supra). Due to its insolubility in most of the solvents, attempts to purify them were not successful.

When $CHCl_3$ was used as a solvent in place of benzene or toluene and refluxing was continued for 2-3 days, the only complex precipitated out of solution was (I). From the filtrate, compound (II), mixed with $[PPh_3NH_2]Cl$ was obtained. (II) was purified by washing it with methanol and ether to remove the impurities of $[PPh_3NH_2]Cl$ and $SPPh_3$ and dried under vacuum.

The same reaction was carried out in xylene. It appeared that the starting compound was decomposed. A mixture of decomposed products was obtained as oil which could not be identified.

(D) When the compound (I)(0.1mmol) was refluxed for 10 hours with 1 ml of pyridine in $CHCl_3$ or benzene (20 ml), no change in

the reaction mixture was observed. The compound (I) was separated from the reaction mixture.

Due to insolubility of the product (I) in most of the solvents, it could not react any further with the ligands.

(2) Effect of Refluxing of [$Ru(NS)Cl_3(AsPh_3)_2$] in different solvents (Benzene, Chloroform)

The procedure of these reactions were similar to those described in (1) except that [$Ru(NS)Cl_3(AsPh_3)_2$] was used in place of [$Ru(NS)Cl_3(PPh_3)_2$] and the refluxing was carried out for about 8 hours. It is only after a long period of refluxing that the dark brown product (III) was crystallised out in a very low yield ($<20\%$), M.P. $>280^\circ C$ (Found: C, 44.5; H, 3.7; N, 2.6; Cl, 14.0; S, 5.0; calcd for $Ru_2Cl_6N_2S_2(AsPh_3)_3$: C, 45.4; H, 3.2; N, 1.9; Cl, 14.8; S, 4.4).

The filtrate was evaporated to about 10 ml under reduced pressure, followed by the addition of petroleum ether whereby a brown shining microcrystalline product was precipitated which was separated by filtration and washed with methanol, ether and analysed for [$Ru(NS)Cl_3(AsPh_3)_2$] (Found: C, 50.2; H, 3.8; N, 2.2; Cl, 13.4; S, 4.4; calcd for [$Ru(NS)Cl_3(AsPh_3)_2$]: C, 49.4; H, 3.3; N, 1.6; S, 3.7; Cl, 12.2), IR: in addition of $AsPh_3$ bands $(\nu_{NS})^+$ 1310 cm^{-1}, m.p. = $>280^\circ C$.

Refluxing of $[Ru(NS)Cl_3(AsPh_3)_2]$ for 2-3 days in the same solvents yielded a mixture of products.

(3) <u>Reactions of $[Ru(NS)Cl_3(EPh_3)(E'Ph_3)]$ (E = P, As; E' = P, As, Sb) with triphenylphosphine</u>

(A) 40 ml of benzene or toluene solution containing $[Ru(NS)Cl_3(EPh_3)(E'Ph_3)]$ (*ca.* 0.25 mmol) and triphenylphosphine (*ca.* 0.6 mmol) was allowed to reflux for 3-4 hours, whereupon the colour of the solution changed from brown to organish-red. The refluxing of the solution continued until red crystals (IV) slowly started separating out at the sidesof flask. These were filtered, washed with benzene, ether and petroleum ether (40-60°) and dried under vacuum (yield, *ca.* 60%) M.P. = 193-7°C (Found: C, 63.0; H, 4.3; N, 1.4; Cl, 11.2; S, 2.4; Calcd for $RuCl_3(PPh_3)_2NSPPh_3$: C, 62.3; H, 4.3; N, 1.3; Cl, 10.2; S, 3.0, IR: in addition to bands due to PPh_3 1380 cm^{-1}, 1100 cm^{-1}, ^1H NMR complicated spectra between δ 7-8. ^{31}P NMR: δ 21.4 ppm, δ 29.1 ppm.

The filtrate was evaporated to dryness, and the residue thus obtained, was dissolved in CH_2Cl_2, followed by the addition of excess petroleum ether to the solution. A grey compound was precipitated, which was separated by filtration, washed with ether, petroleum ether and extracted into ethanol. From the extract, the ethanol was removed under vacuumand the solid residue was recrystallised from CH_2Cl_2/Petroleum ether (40-60°) to give $[PPh_3NH_2]Cl.CH_2Cl_2$. IR: 3100 cm^{-1}, 1120 cm^{-1}.

Refluxing of $[Ru(NS)Cl_3(AsPh_3)_2]$ for 2-3 days in the same solvents yielded a mixture of products.

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When xylene was used instead of benzene or toluene, compound (IV) was obtained in a very low yield. Rest of the solution turned into an oily mass.

The red crystals (IV) on keeping for a long time (1 month or more) in air, lost their lustre. The ir spectrum of this product showed the presence of a broad band at 1300 cm^{-1} besides those of compound (IV).

(B) When the benzene (saturated with H_2O or D_2O) was used in the place of dried benzene, (IV) was not separated from the reaction mixture. Instead the orange microcrystals (V) were precipitated which were filtered, washed with benzene, ether and dried. (Found: C, 60.6; H, 4.1; N, 3.0; Cl, 10.0; S, 3.0; IR: (1315, 1300, 1285, 1265, 1120 cm^{-1}).

The reaction (3) was repeated except the refluxing time was increased to 10-12 hours whereby the orange microcrystalline product (V) was separated.

(C) $[Ru(NS)Cl_3(PPh_3)_2]$, when heated to reflux in chloroform with triphenylphosphine, the product (IV) was not obtained. Instead it yielded a mixture of products which could not be separated, even after repeated attempts to purify them.

(4) Reactions of $[Ru(NS)Cl_3(EPh_3)(E'Ph_3)]$ (E = P, As; E' = P, As, Sb)with triphenylarsine

The procedure for these reactions were similar to those described in (3) except that $AsPh_3$ was used in place of PPh_3. The brown product was separated and analysed. It corresponded to the formula $[Ru(NS)Cl_3(AsPh_3)_2]$ (Found: C, 50.4; H, 3.5; N, 1.2; Cl, 13.0; S, 3.4; Calcd. C, 49.9; H, 3.3; N, 1.6; Cl, 12.2; S, 3.7; IR: $(\nu_{NS})^+ = 1310\ cm^{-1}$ or $[Ru(NS)Cl_3(AsPh_3)(PPh_3)]$(Found: C, 53.5; H, 3.8; N, 1.4; Cl, 13.6; S, 4.2; Calcd for C, 52.6; H, 3.6; N, 1.7; Cl, 12.8; S, 3.8; IR: 1305 cm^{-1}.

(5) Reaction of red crystals (IV) with NOCl

20 ml solution of (0.1 mmol)of (IV) in CH_2Cl_2 was heated to reflux with a saturated dichloromethane solution of NOCl (5 ml) for 2 hours whereby orange crystals of $[Ru(NO)Cl_3(PPh_3)_2]$ were obtained. These were separated by filtration, washed with methanol, ether and dried under vacuum. (Found: C, 55.6; H, 4.2; N, 2.0; Cl, 14.4; Calcd for $[Ru(NO)Cl_3(PPh_3)_2]$: C, 55.1; H, 3.9; N, 1.8; Cl, 13.9; IR: $(\nu_{NO})^+ = 1868\ cm^{-1}$.

The filtrate was evaporated to dryness on a water bath, the residue was washed with diethyl ether and extracted into ethanol. From the extract, the ethanol was removed under vacuum and the solid residue was recrystallised from CH_2Cl_2/light petroleum to give $[PPh_3NH_2]Cl.CH_2Cl_2$. (Found (calcd): C, 57.5 (57.1); H, 5.2 (4.7); N, 4.4 (3.5); Cl, 26.2 (25.3).

(6) Reaction of red crystals (IV) with 2,2'-bipyridine

To a bright orangish-red coloured solution of (IV) (0.1 mmol in $CHCl_3$ (30 ml), 2,2'-bipyridine (0.06 mmol) was added. The reaction mixture was refluxed for 2 hours, whereby orange brown microcrystalline product was obtained. It contained a mixture of products, from which $[RuCl_3(PPh_3)(Bipy)]$ was separated after repeated recrystallitions. M.P. = 220°C (Found (calcd): C, 54.6 (53.7); H, 4.2 (3.6); N, 4.1 (4.4); Cl 16.2 (16.9).

5.3 Results and Discussion

The shining flaky crystals (IV) and those microcrystalline products derived from (IV) were soluble in a number of organic solvents (non-hydrocarbon type) except I and III which were insoluble in most of the organic solvents.

(A) Reactions of $[Ru(NS)Cl_3(EPh_3)_2]$ without adding EPh_3

$[Ru(NS)Cl_3(EPh_3)_2]$ (E = P, As) when heated to reflux in different solvents (Benzene, $CHCl_3$, Toluene, Xylene) yielded diamagnetic insoluble brown compounds I and III. Yield of III (20%) was comparatively lower than that of (I) (increasing the time of refluxing did not have much effect on their percentage yields). Their analytical data corresponded to a dinuclear formula $[Ru_2(NS)_2Cl_6(EPh_3)_3]$. These products did not react with other ligands even

after refluxing for a very long time (24 hours). [Ru(NS)Cl_3-$(EPh_3)_2$] (E = P or As) and free EPh_3 were recovered from their filtrate.

On refluxing the original complexes in xylene, the yields of the products (I and III) were very low (5–10%) and the remaining filtrate afforded an oily mass on slow evaporation from which no compound could be separated after repeated crystallisation. Presumably the compounds were decomposed at the boiling temperature of xylene and formed a mixture of a number of decomposed products as oil.

Their ir spectra displayed a strong sharp band at 1290 cm^{-1} besides the characteristic bands attributed to EPh_3 (E = P or As). No extra band in the 1100 cm^{-1}, 850 cm^{-1} regions were observed. Owing to insolubility of the complexes further physical data for definite structural postulation could not be obtained.

Despite the lack of structural information except those obtained from chemical analyses, magnetic and ir spectral evidence, a tentative structure was however arrived at by a few experimental observations in this direction. Thus, the complexes [Ru(NS)Cl_3-$(EPh_3)_2$], being monomeric with two EPh_3 molecules bonded trans to each other,[5] should exhibit trans effect ($PPh_3 > AsPh_3$), resulting in the dissociation of one EPh_3 molecule with the formation of a five coordinate species [Ru(NS)Cl_3EPh_3] or solvated product. The five coordinated species being coordinatively unsaturated, will

have a remarkable tendency to become hexacoordinated and thus, may form bridge via chloro atom of undissociated molecule of $[Ru(NS)Cl_3(EPh_3)_2]$ to afford a dinuclear structure. The relatively higher trans effect of PPh_3 (kinetic phenomenon) than $AsPh_3$, should result in the higher formation rate of the brown complex (I) than that of complex (III) which is in concordancewith the observation. Another supportive evidence in favour of proposed bridged structure is, the absence of any extra band around 1100 cm^{-1}, 800 cm^{-1}, 600 cm^{-1} suggesting no effect on the bonded NS moiety. Furthermore, these complexes were diamagnetic and have the position and the shape of (ν_{NS}) band in their ir spectra exactly similar to those exhibited by the spectra of their parent molecule. (The ir spectra of the brown complexes were identical to those of $[Ru(NS)Cl_3(EPh_3)_2$

Another major problem that one encounters in the present case is, why does highly thiophilic PPh_3 formed during the trans elimination not attack on an electrophilic sulphur atom of the bonded NS.[7-10] The latter interaction was observed during the reactions of $[Ru(NS)Cl_3(EPh_3)_2]$ with PPh_3 or $AsPh_3$ (vide supra). The explanation could be, the very low concentration of EPh_3 in solution because of which the rate of the nucleophilic attack on sulphur, will be very slow and at the same time, the five coordinated species will simultaneously interact with $[Ru(NS)Cl_3(EPh_3)_2]$ with a sequential formation of the dinuclear product. The latter, being insoluble, will remove the undisturbed bonded NS compound from the reaction medium. It has, however, been observed that

refluxing the solution along with the insoluble material for a much longer time (8 hours) yielded a product from the solution whose ir spectrum did exhibit some signs of attack by EPh_3 on the NS group.

Another probe in this direction is the lower trans effect of $AsPh_3$ compared to that of PPh_3. The observed rate of formation of complex III was found to be slower than that of complex I becaus of lower effective concentration of $AsPh_3$.

The above observations along with the evidence from ir spect-ral and analytical data suggested $[Ru(NS)Cl_3(EPh_3)\text{-}Cl\text{-}Ru(NS)Cl_2\text{-}(EPh_3)_2]$ as a possible formula of the complexes.

(B) Reactions of $[Ru(NS)Cl_3(EPh_3)(E'Ph_3)]$ (E = P, As; E' = P, As Sb) with EPh_3 (E = P, As) in different solvents (Benzene, Toluene)

When $[Ru(NS)Cl_3(EPh_3)(E'Ph_3)]$ was allowed to react with PPh_3 in refluxing dry benzene or toluene, initially a red coloured solution was obtained from which orange-red coloured shining crystalline flakes (IV) subsequently appeared on the sides of flask. These were soluble in chloroform, dichloromethane and insoluble in hydrocarbons and analysed as $[Ru(NS)Cl_3(PPh_3)_3]$ To arrive at a suitable structural formula of the complex, the following experimental results were considered.

(1) The complex could be preserved for a couple of months and it slowly changes to some other products on keeping. No change in the complex was however observed on keeping for a few days.

(2) Reaction of (IV) with NOCl in chloroform led to the isolation of $[Ru(NO)Cl_3(PPh_3)_2]$. However, if the same complex was treated with bipyridyl, $[RuCl_3(PPh_3)(bipy)]$ was obtained. Both the complexes $[Ru(NO)Cl_3(PPh_3)_2]$ and $[RuCl_3(PPh_3)(bipy)]$ were isolated and characterized by comparing them with the authentic samples.

(3) The ir spectrum of (IV) exhibited bands at 1380 cm^{-1} (sharp) 1100 cm^{-1} (medium), three bands of strong to medium intensity in the regions 740–680 cm^{-1} and 530–500 cm^{-1}.

(4) ^{31}P spectrum of (IV) displayed two sharp resonance peaks at δ 21.4 and δ 29.1 ppm.

(5) Complex IV was found to be paramagnetic corresponding to one unpaired electron (μ_{eff} = 1.7 BM).

(6) Its esr spectrum in $CHCl_3$ exhibited a broad signal corresponding to the average $\langle g \rangle$ value of 1.95.

(7) On refluxing $[Ru(NS)Cl_3(EPh_3)(E'Ph_3)]$ with PPh_3 for a period longer than 8–10 hours or in benzene saturated with H_2O or D_2O, compound V was obtained whose ir spectrum exhibited slow disappearance of the 1380 and 1100 cm^{-1} bands and new bands

appeared in 1320 - 1260 cm^{-1} region (broad) and 1120 cm^{-1}. Furthermore, from the filtrate of the reaction medium, $[Ph_3PNH_2]Cl$ and $SPPh_3$ were recovered. ^{31}P NMR of (V) displayed a number of resonances in the region corresponded to: δ 21.4 (PPh_3); δ 25.4 (PPh_3NH); δ 40.7 ($SPPh_3$).

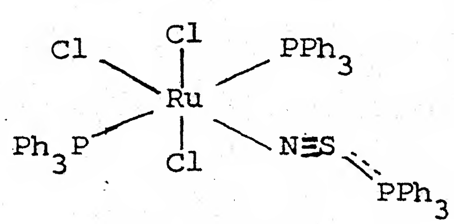
(8) Both the compounds IV and V showed complicated resonance peaks in their ^{1}H nmr spectra in the δ 7-8 ppm region.

(9) Interestingly, no compound similar to (IV) was formed when $[Ru(NS)Cl_3(AsPh_3)_2]$ was heated to reflux with excess $AsPh_3$. However, if $[Ru(NS)Cl_3(AsPh_3)_2]$ was refluxed with PPh_3, the red compound (IV) was isolated. Refluxing of $[Ru(NS)Cl_3$-$(PPh_3)_2]$ with $AsPh_3$ led to the substitution of PPh_3 by $AsPh_3$ yielding $[Ru(NS)Cl_3(AsPh_3)(PPh_3)]$.

(10) The electronic spectrum of the complex exhibited a weak band at 550 nm (ϵ = 400), 460 nm (ϵ = 940) and 380 nm (ϵ = 2090) besides the ones arising out of EPh_3 in the UV region.

(11) When $[Ru(NS)Cl_3(PPh_3)_2]$ was refluxed with triphenylphosphine in $CHCl_3$ or CH_2Cl_2, the product (IV) was not obtained.

The results, described in the preceeding paragraph may be explained, if the following model is chosen for the tentative structure of complex (IV).



According to this model the thiophillic nucleophile PPh_3, present in excess in solution attacks on the electrophile sulphur of the bonded NS.[7-10] The nature of the attack is similar to the one already well established in the literature[11,12] for a number of N-S compounds. It is presumed that the bond between P and S is not a double one like that in $S{=}PPh_3$. Though it is not possible to know exactly the nature of this bond, but one can think $-N{\equiv}S{-}PPh_3$ bond order as one similar to S-Cl bond in $-N{\equiv}S{-}Cl$ complexes in which it acts as a neutral ligand and whose i.r. spectrum display bands in the 1380-1300 cm^{-1} region.[13-16] The attack of PPh_3 at S will shift the position of (ν_{NS}) towards higher wave numbers in the i.r. spectrumof the complex IV as observed. The presence of three strong bands around 740-680 cm^{-1} and 530-500 cm^{-1} also indicate a different environment of three phenyl groups of PPh_3 bonded to sulphur of NS. The latter observation is also confirmed by the results of the positions of ^{31}P NMR bands, exhibiting two non-equivalent environments around phosphorus in the complex. Two PPh_3 molecules bound in the trans position to the metal may give rise to a single sharp peak at δ 21.4 ppm. Its downfield shift compared to that in $[Ru(NS)Cl_3(PPh_3)_2]$ (δ 13.3 ppm)[17] may arise owing to greater polarization of electron density of P in bonded PPh_3 towards the metal ion in +3 oxidation state compared to one in +2 state with consequent more deshielding of phosphorous. The other triphenylphosphine coordinated to sulphur atom showed the

resonance at δ 29.1 ppm. The resonance in $S{=}PPh_3$ occurs at δ 43.2 ppm [18] suggesting the bond order of P–S bond to be lower than two as obvious from our model.

When $[Ru(NS)Cl_3(PPh_3)_2]$ was refluxed without PPh_3 for a longer time (2–3 days) in benzene, the product (IV) was obtained together with the major product (I). It suggested that the PPh_3 molecule which comes out in the system by trans effect, reacted with coordinated NS very slowly owing to very low concentration of triphenylphosphine in the reaction medium.

The reactions of $[Ru(NS)Cl_3(AsPh_3)_2]$ yielded no compound analogous to the product (IV). The reason for this behaviour could be lower nucleophilicity of $AsPh_3$. Thus, possibly $AsPh_3$ is not a sufficiently strong base to attack on the sulphur atom and the $[Ru(NS)Cl_3(AsPh_3)_2]$ is recovered as such from the reaction mixture.

The electronic spectra of $[Ru(NS)Cl_3(PPh_3)_2]$ did not display the band around 600 nm. Generally $[RuCl_3(PPh_3)_2]$ showed absorption at 600 nm, 420 nm and 350 nm[19] whose positions are similar to the ones displayed by the electronic spectrum of (IV). The absorption around 460 nm and 380 nm were assigned to LMCT. The more intense absorption in the UV region are assigned to intra ligand transitions super-imposed on charge transfer bands arising from the PPh_3 molecule. The band around 550 nm in (IV) also indicated the presence of +3 state of Ru in it. It suggested that the complex IV

possibly has $[RuCl_3(PPh_3)_2]$ moiety. The latter proposition was also supported by the fact that the reactions of (IV) with NOCl yielded $[Ru(NO)Cl_3(PPh_3)_2]$[20] and with bipyridyl $[RuCl_3(PPh_3)$-bipy][19].

Ruthenium is in +3 oxidation state was also suggested by its magnetic moment corresponding to one unpaired electron which is also corroborated by the ⟨g⟩ value of 1.95 in its ESR spectra. T value is slightly on the lower side possibly due to the lower symmetry of the complex and high covalency in the bonds.

Once bond between P of PPh_3 and sulphur is formed in (IV) to yield an unstable system ($-N{\equiv}S-PPh_3$), one or more than one of the following rearrangements in the complex may take place.
(a) The bonds in $N{\equiv}S-PPh_3$ rearrange to $Ru-N=S=PPh_3$ group (which gets either polymerized and/or forms ring compounds). Thus it is possible to get a number of compounds containing N, S, P from the $Ru-N{\equiv}S-PPh_3$ moiety depending upon the rearrangement of the bonds. One should therefore expect a complicated pattern in the spectra (ir, ^{31}P and ^{1}H) which is in concordance with the observed data. Unfortunately, it is impossible to comment on the exact nature of bond formation after $Ru-N{\equiv}S-PPh_3$ starts decomposing. (b) PPh_3 pulls out sulphur to yield $SPPh_3$ and subsequently another PPh_3 molecule attacks on nitrogen of $Ru-\ddot{N}:$ yielding $PPh_3=\ddot{N}$ followed by its protonation to finally yield $[PPh_3NH_2]^+Cl^-$.

In retrospect one may conclude that initially PPh_3 is attacking on the sulphur of bonded NS group yielding a complex in which the bonds further rearrange to either $\rangle N{-}S{=}PPh_3$ (less probable), from which PPh_3 pulls out sulphur yielding $SPPh_3$ and $[PPh_3NH_2]^{+}Cl^{-}$ or which gets polymerized to yield ring compounds or polymers. Though it is very difficult to comment about the final products but it seems fairly certain that initially nucleophilic attack of PPh_3 on sulphur of NS takes place which subsequently yields a number of products, $SPPh_3$ and $[PPh_3NH_2]^{+}Cl^{-}$. It needs more work to suggest the structural arrangement of ligands around the metal center after rearrangements of the bonds in $[RuCl_3(PPh_3)_2NS{-}PPh$

CAPTIONS FOR THE FIGURES

Infrared spectra of the complexes.

Fig. 5.1 $[Ru(NS)Cl_3(EPh_3)\text{-}Cl\text{-}Ru(NS)Cl_2(EPh_3)_2]$

Fig. 5.2 (1) $[RuCl_3(PPh_3)_2(NSPPh_3)]$

(2) $[RuCl_3(PPh_3)_2(NSPPh_3)]$ - after keeping it for one month.

(3) $[RuCl_3(PPh_3)_2(NSPPh_3)]$ - after 6-7 hours of refluxing

(4) Compound V

^{31}P NMR spectra of the complexes

Fig. 5.3 (a) $[RuCl_3(PPh_3)_2(NSPPh_3)]$

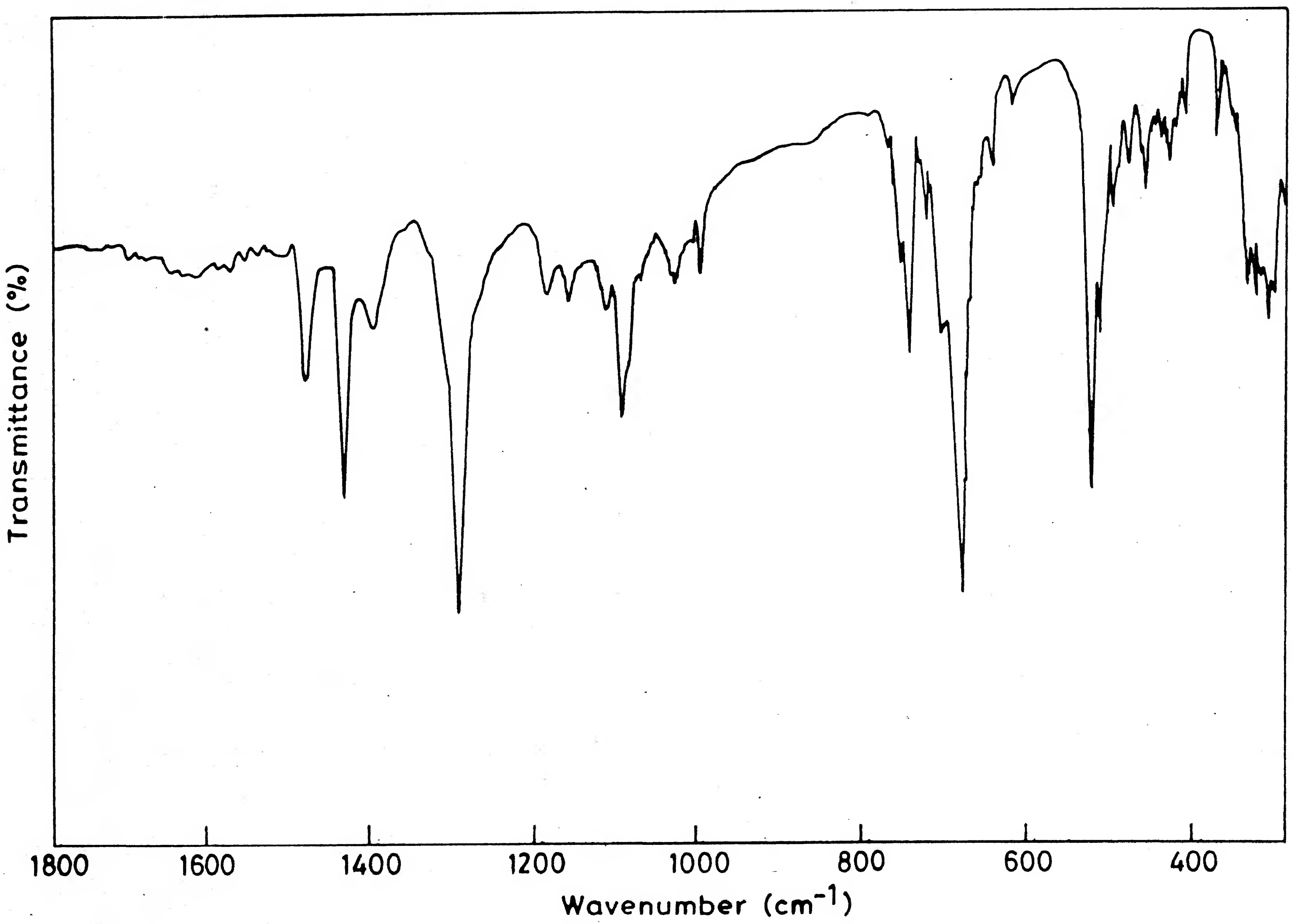
(b) Compound V

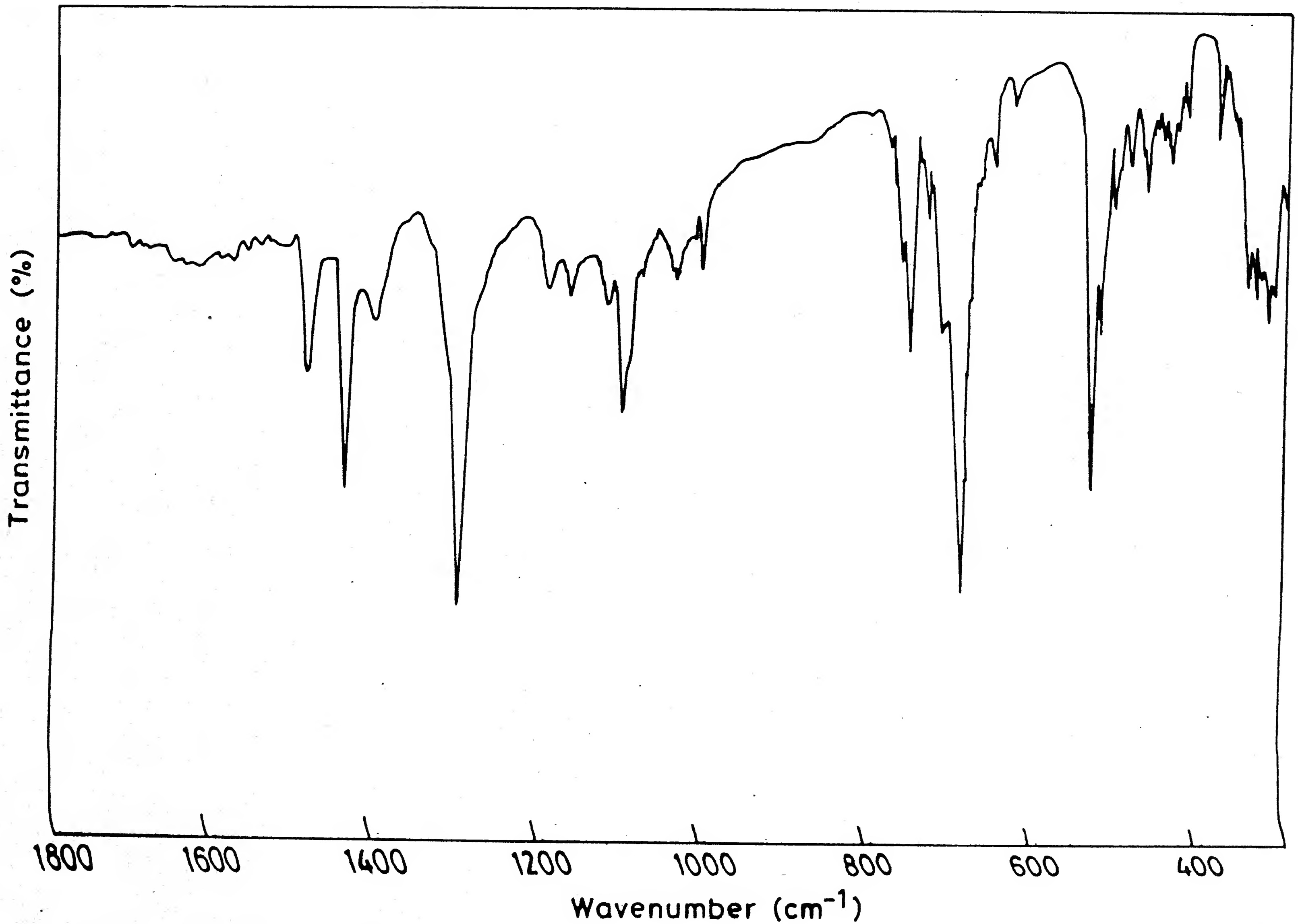
ESR spectrum of the complex

Fig. 5.4 $[RuCl_3(PPh_3)_2(NSPPh_3)]$

Electronic spectra of the complex

Fig. 5.5 $[RuCl_3(PPh_3)_2(NSPPh_3)]$


Transmittance (%)
1800
1600
1400
1200
1000
800
600
400
Wavenumber (cm^{-1})


Transmittance (%)
1800
1600
1400
1200
1000
800
600
400
Wavenumber (cm⁻¹)

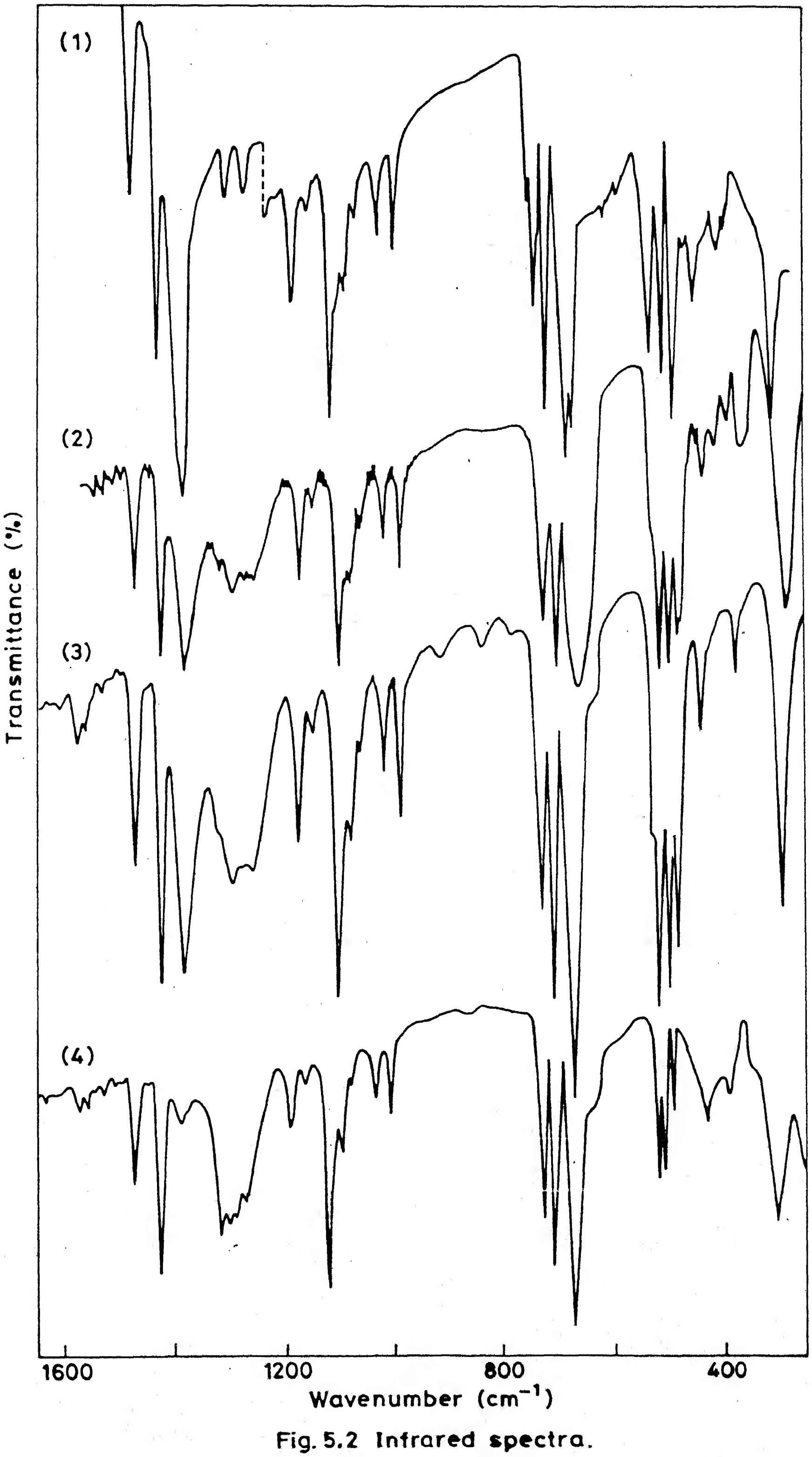


Fig. 5.2 Infrared spectra.

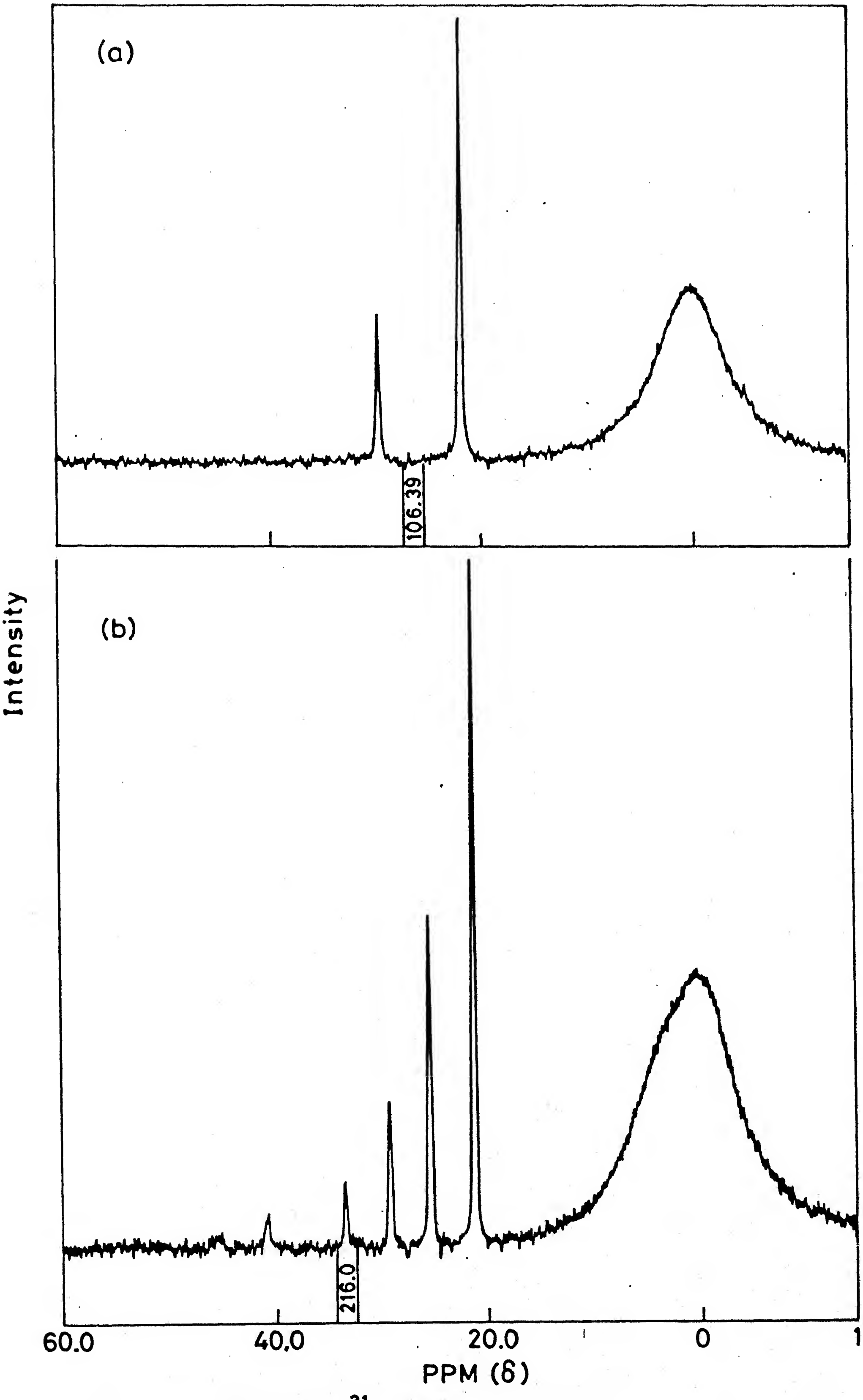


Fig. 5.3 ^{31}P NMR spectra.

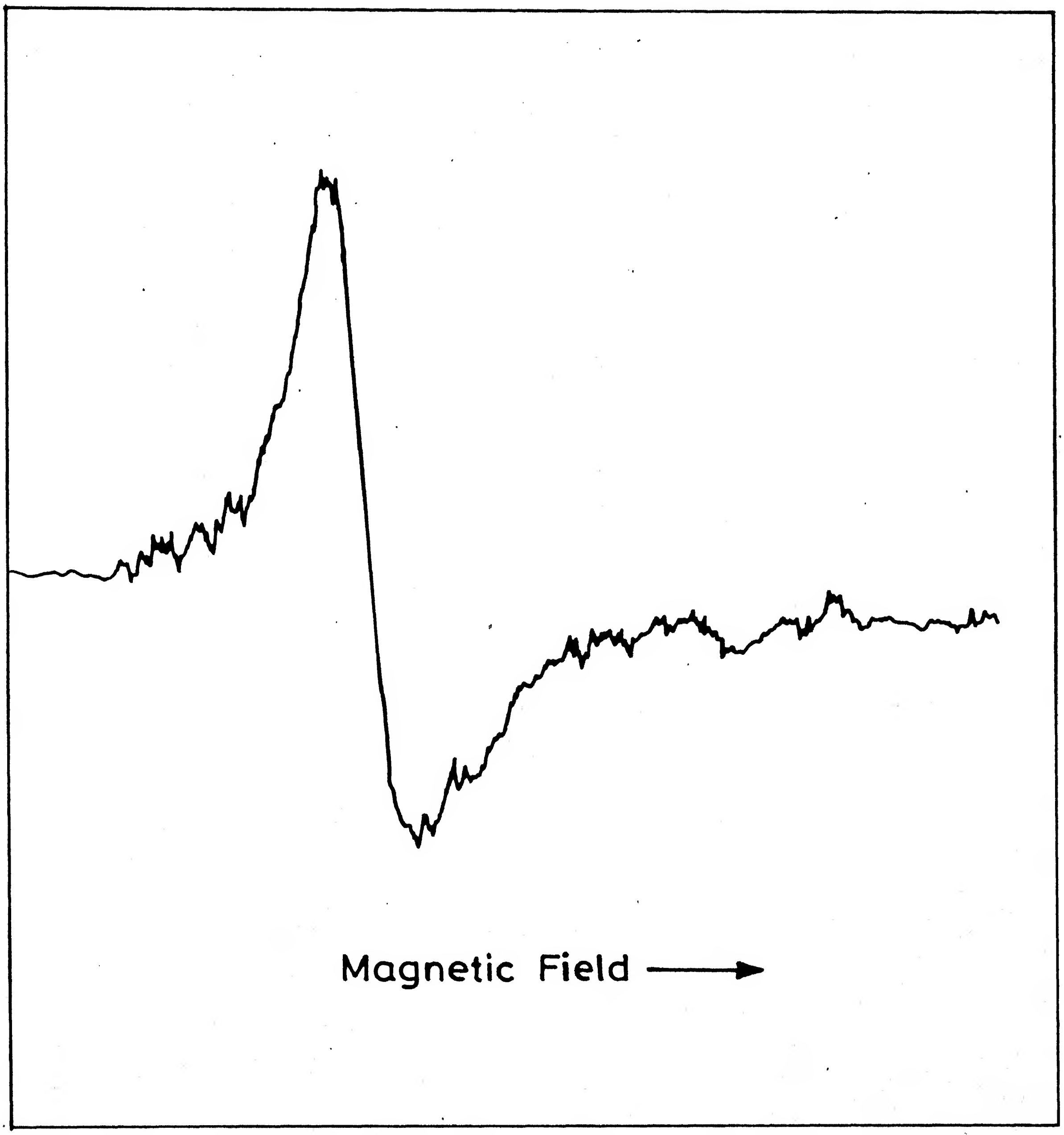


Fig. 5.4 E.S.R. spectrum.

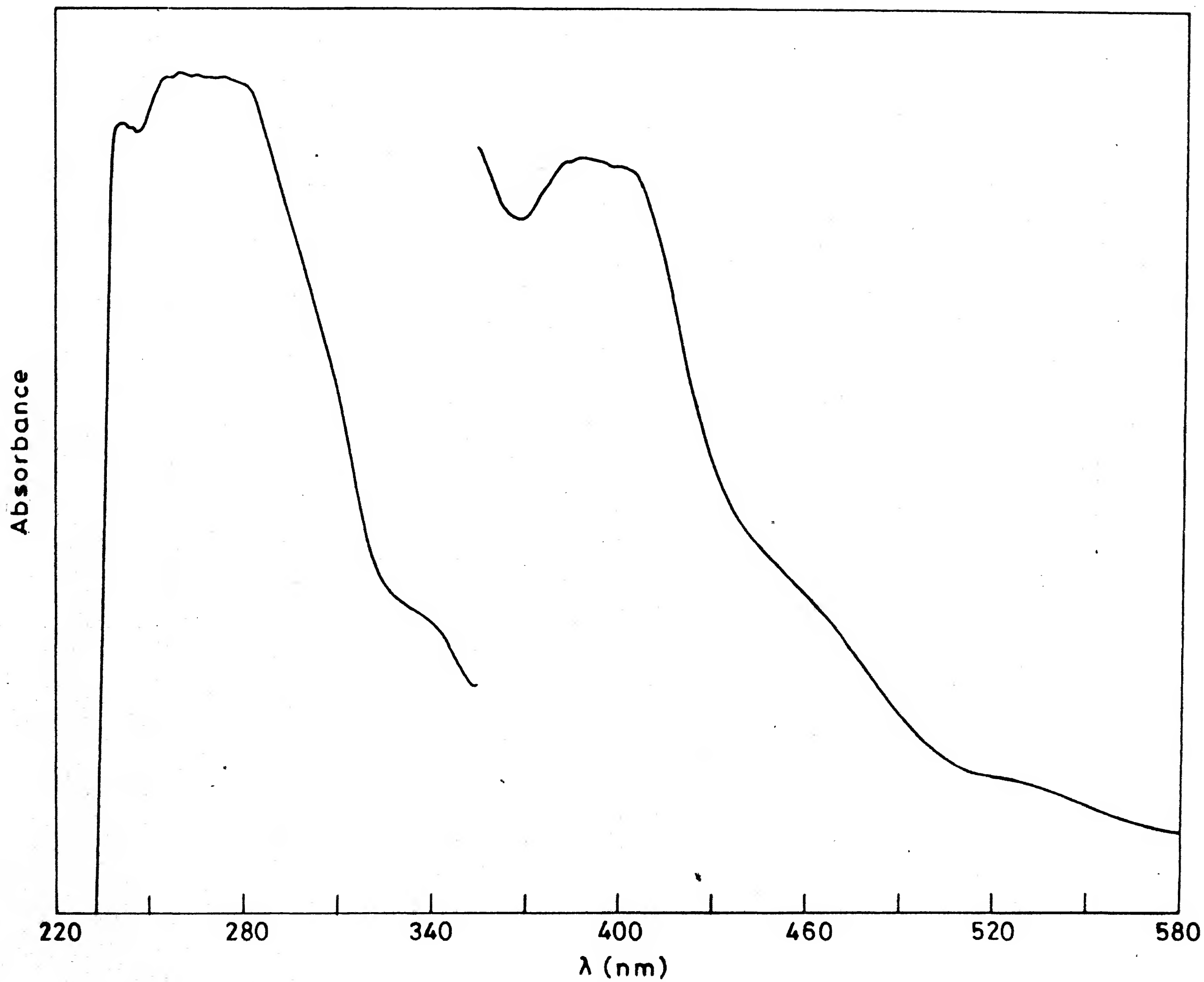


Fig. 5.5 Electronic spectra.

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Chapter – VI

Summary and Scope for Future Work

A survey of past fifteen years literature abundantly supports the synthetic versatility and the range of unusual chemistry displayed by cyclopentadienyl bis triphenylphosphine ruthenium(II) $[Ru(\eta^5-C_5H_5)X(PPh_3)_2]$ and its derivatives. The amount of work on these compounds matches equally with that carried out on the reactivities and structure elucidations of ruthenium nitrosyls. In addition, there is no known complex of $[Ru(\eta^5-C_5H_5)-X(EPh_3)_2]$ (E = P, As, Sb) in which one or more of the ligand molecules have been substituted by a nitrosyl group. Since nitrosylation reaction falls within our interest, interactions of NOX (X = Cl^-, Br^- or Br_3^-) with $[Ru(\eta^5-C_5H_5)X(EPh_3)_2]$ (E = As, Sb) and its substituted complexes have, therefore, been attempted.

Although literature reveals a large number of ruthenium nitrosyl complexes, only a few analogous thionitrosyl complexes were known as yet. Limited applications of trithiazyltrichloride have been known, as a thionitrosylating agent for the synthesis of a few metal thionitrosyls. Furthermore, no work has been carried on the chemical reactivity of N and/or S of the coordinated NS group. It was, therefore, felt interesting to look into the substitution reactions of metal complexes with $N_3S_3Cl_3$ and the reactions of various nucleophiles and electrophiles towards metal thionitrosyls.

First chapter of the thesis describes, in brief, the scope and objectives of the work, followed by a comprehensive, yet a compact, review of nitrosyl chemistry. It consists of the synthesis, reactions and the bonding modes of transition metal nitrosyls. This is followed by a brief overview of the chemistry of metal thionitrosyls in which synthesis, reactivity and the bonding modes of metal thionitrosyls have been emphasized.

The details of the reactions of NOX (X = Cl^-, Br^- or Br_3^-) with η^5-cyclopentadienyl ruthenium(II) complexes of type $[Ru(\eta^5-C_5H_5)(EPh_3)L-L]^+X^-$ (where E = As, Sb; L-L = 2,2'-Bipyridine, 1,10-phenanthroline; X = Cl^-, Br^-, I^-, CN^-, NCS^-) and $[Ru(\eta^5-C_5H_5)(EPh_3)LX]$ (E = As, Sb; L = $AsPh_3$, $SbPh_3$, PPh_3, Pyridine, γ-Picoline; X = Cl^-, Br^-, I^-, CN^-, NCS^-) are given in chapter II. The reaction products were mixed ligand nitrosyl complexes of type $[Ru(NO)XX'_2(EPh_3)L]$ (X' = Cl^-, Br^-) and $[Ru(NO)XX'(EPh_3)L-L]X'$ (X' = Cl^- or Br^-). The nitrosyl products were isolated with the loss of η^5-cyclopentadienyl moiety from the coordination sphere during nitrosylation. In all the complexes the NO group binds as NO^+ with the metal (a terminal and linear mode of bonding). The starting compounds which have CN^- or NCS^- as coligands, yielded the solid products containing CN or NCS only in a few cases, after the reactions with NOX. In the remaining cases the solid products were obtained where CN^- or NCS^- were substituted by Cl^- or Br^-, only after the addition of a small amount of $AsPh_3$ or $SbPh_3$ in the reaction mixture. The

reactivities of $[Ru(\eta^5-C_5H_5)X(EPh_3)_2]$ (E = As, Sb) towards NOX were different from those of $[Ru(\eta^5-C_5H_5)X(PPh_3)_2]$. This has been explained in terms of the differences in the π-acceptor and oxidation properties of $AsPh_3$ and $SbPh_3$ from that of PPh_3. The rate of the formation of nitrosyl complexes decreased in the order $PPh_3 > AsPh_3 > SbPh_3$. Addition of $AsPh_3$ or $SbPh_3$ in the reaction mixture was necessary for the better yield of the reaction products.

Chapter III describes the details of the reactions of $[Ru(\eta^5-C_5H_5)SnCl_3(EPh_3)L]$ (E = As, Sb; L = $AsPh_3$, $SbPh_3$, PPh_3, Pyridine, γ-Picoline) and $[Ru(\eta^5-C_5H_5)(EPh_3)L\text{-}L]SnCl_3$ (E = As, Sb; L-L = 2,2'-Bipyridine, 1,10-phenanthroline) with NOX (X = Cl^-, Br^- or Br_3^-). Although the role played by strong π-acids, like $SnCl_3$ in changing the course of reactions is still obscure; however the reaction path is dependant upon the various electronic and/or steric factors of reactants. The reaction products of these reactions were explained in terms of two parallel reactions occurring simultaneously. These are (1) reactions leading to nitrosyl formation and (2) reactions leading to the formation of complexes in which one of the phenyl rings of EPh_3 ligand binds through its π-electrons with the metal center and NO is oxidized to NO_2. The ratio of the formation of nitrosyl complexes with π-bonded ones in the case of complexes with triphenylphosphine as coligands is 1:8 while it just reverses in triphenyl

stibine complexes. Interaction of $[Ru(\eta^5-C_5H_5)SnCl_3(EPh_3)(E'Ph_3)]$ (E = As; E' = As, P) with NOX led to the formation of red products which exhibited bands due to ν_{NO}, ν_{NO_2}, π-bonded phenyl group and phenyl groups in their IR spectra. Addition of EPh_3 to the reaction mixture yielded $[Ru(NO_2)SnCl_3(EPh_3)(\pi-C_6H_5)EPh_2)$ and $[Ru(NO)X_3(EPh_3)_2]$. Reactions of $[Ru(\eta^5-C_5H_5)SnCl_3(SbPh_3)_2]$ with NOX gave $[Ru(NO)(NO_2)_2Cl(SbPh_3)]$ and if $SbPh_3$ was added to the reaction mixture, $[Ru(NO)X_3(SbPh_3)_2]$ and $[Ru(NO_2)SnCl_3(SbPh_3)(\pi-C_6H_5)SbPh_2]$ were isolated in the ratio of 8:1. The difference in their behaviour towards the π-complex formation parallels the σ-basicity of phosphine, arsine and stibine ($PPh_3 > AsPh_3 > SbPh_3$). NO_2^-, $SnCl_3^-$, EPh_3 are π-acids and their π-acidity appears to have an important role in the formation of π-bonded complexes. This may further explain the decreasing order of the π-bonded complex formation in these reactions ($PPh_3 > AsPh_3 > SbPh_3$). (The π-acid character increases in the following order $SbPh_3 < AsPh_3 < PPh_3$).

The reactions of $[Ru(\eta^5-C_5H_5)(EPh_3)L-L]SnCl_3$ and $[Ru(\eta^5-C_5H_5)SnCl_3(EPh_3)L]$ (E = P, As) with NOX led to the formation of π-bonded complexes in very low yield. From the filtrate the isolated products were $[Ru(NO)(NO_2)X_2L-L]$ ($X = Cl^-, Br^-$) and $[Ru(NO)X_3(EPh_3)L]$. The reactions with $SbPh_3$ complexes having heterocyclic ligands did not yield any π-bonded product. Instead, the products obtained were $[Ru(NO)X_3L-L]$ and $[Ru(NO)X_3(EPh_3)L]$.

Chapter IV gives an account of the reactions of trithiazyl trichloride with Ru(III) complexes of the type $[RuCl_3(EPh_3)_2S]$ (E = P, As; S = CH_3CHO, CH_3CN, CS_2, THF, DMSO, DMF, $(CH_3)_2CO$) which on further reaction with triphenylphosphine, triphenylarsine, triphenylstibine or zinc yielded $[Ru(NS)Cl_3(EPh_3)(E'Ph_3)]$. These reactions were slightly complicated, possibly they undergo through an intermediate state which we presumed to be coordinatively unsaturated Ru(III) complex, followed by the formation of a coordinatively saturated complex by linking with the ligands like PPh_3, $AsPh_3$ or $SbPh_3$. Furthermore, the reactions of $[Ru(NS)Cl_3(EPh_3)(E'Ph_3)]$ (E = P, As; E' = P, As, Sb) with $E''Ph_3$ (E'' = P, As, Sb) afforded complexes of the type $[Ru(NS)Cl_3(EPh_3)(E''Ph_3)]$ or $[Ru(NS)Cl_3(E''Ph_3)(E''Ph_3)]$. The order of the ligand exchange rate is in the order $PPh_3 < AsPh_3 < SbPh_3$. Another point of importance regarding the substitution of EPh_3 could be that of steric hindrance or the trans effect of EPh_3 which is in the order ($PPh_3 > AsPh_3 > SbPh_3$).

Substitution reactions of $[Ru(NS)Cl_3(EPh_3)(E'Ph_3)]$ with the heterocyclic bases (L), viz. pyridine, γ-picoline, pyrazine, pyrazole afforded the complexes $[Ru(NS)Cl_3(EPh_3)L]$ or $[Ru(NS)Cl_3(E'Ph_3)L]$.

In chapter V the details of the reactions of EPh_3 (E = P, As) with the coordinated NS group of $[Ru(NS)Cl_3(EPh_3)_2]$ (E = P, As) have been presented with a view to study the nucleophilic

attack of EPh_3 on the sulphur (electrophile) in benzene and other non-coordinating solvents. Interestingly, the reaction of [Ru(NS)-$Cl_3(EPh_3)(E'Ph_3)$] with PPh_3 resulted in the isolation of red crystals [$RuCl_3(PPh_3)_2NSPPh_3$] which were paramagnetic in nature and contain two non-equivalent triphenylphosphine molecules in the complex as has been confirmed by ^{31}P NMR and IR spectrum. The nucleophilic PPh_3 when present in excess in the solution, attacked on sulphur of the bonded NS group and possibly formed $-N\equiv S-PPh_3$ type of bonding (owing to this attack the position of (ν_{NS}) band will be shifted towards higher wave number like in $-N\equiv S-Cl$). On further refluxing, the red crystals in benzene or the formation of red crystals in benzene (saturated with H_2O or D_2O) yielded orange coloured flakes having possibly no NS group bonded to Ru center. It suggested that the system $-N\equiv S-PPh_3$ (unstable) rearranged on further refluxing or in presence of H_2O formed either $Ru-N=S=PPh_3$, or got polymerized and/or formed ring compounds of P, N and S.

The reactions of [$Ru(NS)Cl_3(AsPh_3)_2$] with $AsPh_3$ yielded no compound analogous to the product [$RuCl_3(PPh_3)_2(NSPPh_3)$], instead [$Ru(NS)Cl_3(AsPh_3)_2$] was isolated. The reason could be the lower nucleophilicity of $AsPh_3$ as compared to PPh_3.

Reactions of [$Ru(NS)Cl_3(EPh_3)_2$] (E = P, As) in various solvents (C_6H_6, $CHCl_3$, Toluene, Xylene) yielded diamagnetic dimeric insoluble brown complexes having a formula [$Ru(NS)Cl_3EPh_3$-Cl-Ru(NS)-$Cl_2(EPh_3)_2$]. The higher trans effect of PPh_3 than $AsPh_3$, resulted

in the better yield in the case of the triphenylphosphine complex as compared to that of triphenylarsine one.

The work described in the thesis could be further extended in the following directions:

(a) The novel conversion of NO to NO_2 in $SnCl_3$ complexes during nitrosylation also provide good scope for future studies. This conversion of NO to NO_2 has relevance in environmental pollution control and also in organic synthesis.

(b) In this work, it is observed that the η^5-C_5H_5 moiety invariably is lost from the coordination sphere during nitrosylation. A number of C_5Me_5 complexes with Pt metals are known, and in which C_5Me_5 seems to show far lesser tendency to dissociate from coordination sphere, so their activation behaviour towards NO could be studied.

(c) Since the trichlorostannate complexes seem to accomplish the conversion of NO to NO_2 in a very facile way under homogeneous reaction conditions, the possible activation of CO to CO_2 by a similar manner could also be investigated in future.

(d) The arene ruthenium(I) complexes $[Ru(\eta^6-C_6H_6)(PPh_3)X_2]$ is so far little studied as to its reaction with nitrosylating agents. This could be taken up to widen the understanding of this particular area of organo ruthenium chemistry.

(e) Photochemical activation studies of these complexes could also be carried out.

(f) Synthesis of S-bonded thionitrosyl complexes.

(g) Studies on the reactions of coordinated thionitrosyl group.